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INTEGRATED CRITERIA DOCUMENT CHROMIUM

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Mailing list integrated criteria document Chromium

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CONTENTS

SUMMARY

This document on the subject of chromium contains data concerning its sources and distribution pattern (soil, water, air, biota), the risks based on a careful consideration of exposure levels and toxic concentrations, the technical possibilities of reducing these risks and the financial consequences for the industries concerned of any measures to be taken.

Chromium belongs to the heavy metals and is used in the Netherlands chiefly in the form of chromium chemicals in various industrial sectors (about 1000 tonnes of Cr(III)/Cr(VI) and about 750 tonnes of Cr(VI) per year). Approximately 1150 tonnes are dumped annually, about 200 tonnes are emitted directly into the environment, and the remainder enters the economy and is incorporated into chemical waste. Figure A summarizes the chromium emissions from sources in the Netherlands, the contributions from abroad, and the flows and accumulation of chromium in the Dutch environment. With regard to emissions into air, a distinction has been made between Cr(III) (about 4 tonnes per year) and Cr(VI) (about 1 tonne per year) because of the difference in toxic effects of these two species. This figure shows that the contribution made by foreign sources to the chromium load in the Dutch environment is large: up to approximately 90% to the ambient air concentrations and about 94% to the concentrations in the freshwater basins. The chromium input to the soil, however, is determined mainly by emissions in the Netherlands, especially those from the agricultural sector. The soil accumulates a total of about 90 tonnes per year, which corresponds to an annual increase in the soil chromium level of 10-20 $\mu g.kg^{-1}$. This increase is of little significance in view of the concentration values in the soil (11-164 $mg.kg^{-1}$).

Environmental quality standards for this heavy metal exist (or are being initiated) in the Netherlands for soil and water, but not yet for ambient air. The reference value in force for soil and groundwater is generally not exceeded. The current concentrations in surface waters are well below the basic quality level. In sediments and some water meadows and polders covered with harbour sludge, however, the tolerable level and occasionally even the limit value are exceeded because of the larger chromium input in the past.

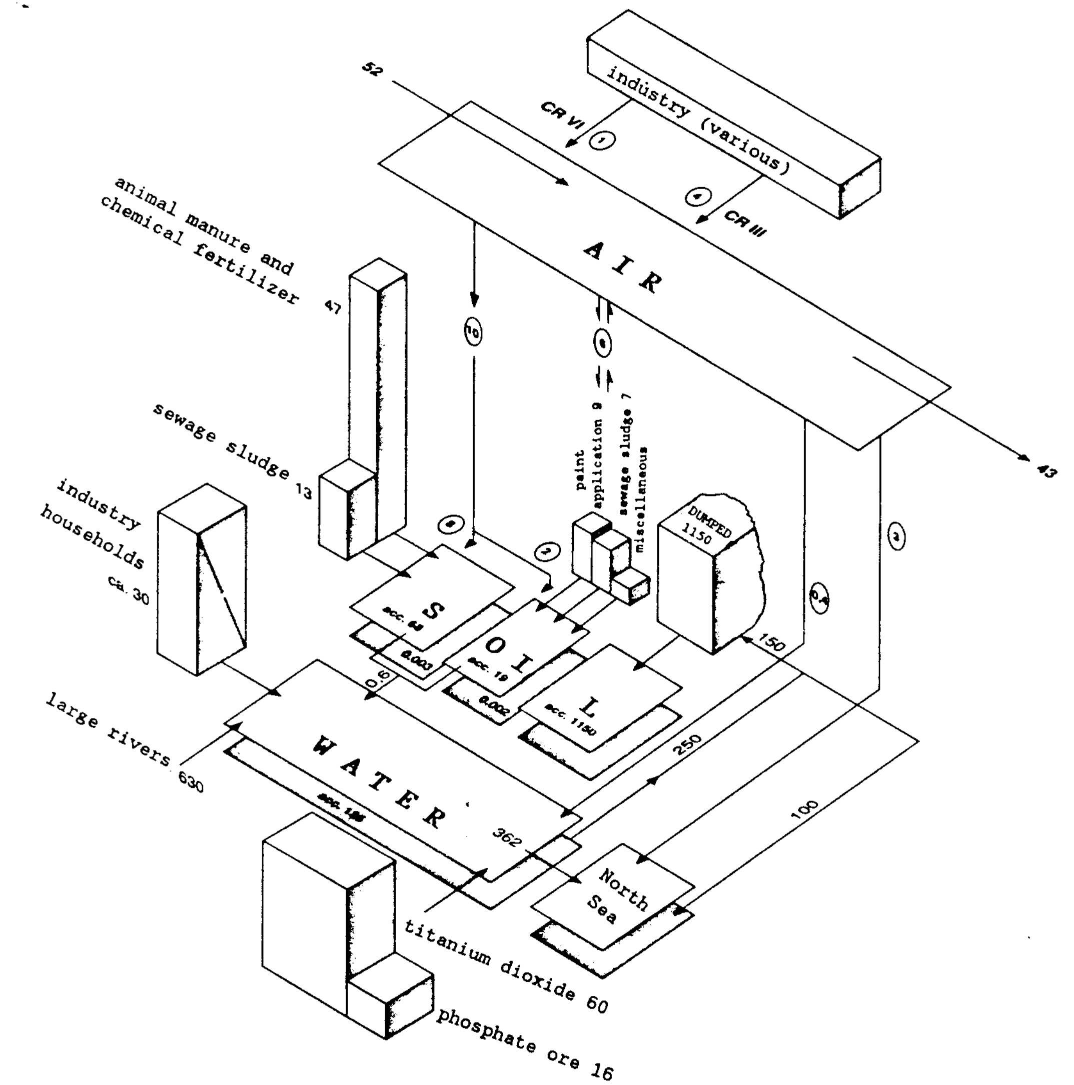

Figure A: *Schematic summary of the chromium emissions in the Netherlands, the contributions from abroad, and the flows and accumulation of chromium in the Dutch environment*

Annual chromium emissions into the air total about 5 tonnes, and about 52 tonnes per year are imported into the Netherlands from abroad. Of these 57 tonnes of chromium, 10 and 3-4 tonnes are deposited on the soil and in fresh/salt surface waters respectively, the remaining 43 tonnes being again exported via aerial transport. Approximately 6 tonnes circulate in the air as a result of windblown dust.

The chromium input to agricultural soils from the application of animal manure, chemical fertilizer and sewage sludge totals about 60 tonnes, which, together with 8 tonnes contributed by deposition, results in an accumulation of about 68 tonnes per year. The annual input to non-agricultural soils is about 19 tonnes, virtually all of which also accumulates.

Approximately 30 tonnes of chromium are released into fresh surface waters through wastewater effluents from industrial sources and households (leaching - 0.6 tonne - is negligible); a number of important sources discharge chromium into the Nieuwe Waterweg (a total of 76 tonnes per year). The transboundary input is 630 tonnes per year. The total input is therefore about 730 tonnes, of which approximately half is carried to the North Sea, about 135 tonnes accumulate in sediments, while around 250 tonnes are dredged and dumped partly on land and partly in the sea.

With regard to the effects of chromium in man, a distinction should be made between oral exposure and exposure by inhalation, and also between the two forms of occurrence of chromium in the environment, Cr(III) and Cr(VI). Chromium is an essential trace element for man: the minimum daily requirement is estimated at 30-130 ng Cr(III).kg^{-1} body weight per day. The main intake source of Cr(III) is the diet [1600 (range 800-3200) ng Cr(III).kg^{-1} body weight per day]; inhaled Cr(III) contributes a negligible amount to the total intake [0.02-0.06 ng Cr(III).kg^{-1} body weight per day]. Maximum permissible levels for man are not known, but the maximum human intake is at least 150 times lower than the no-effect dose established in animal experiments. Therefore the range of Cr(III) concentrations ingested by man in food and water lies between the minimum requirement and the toxicologically maximum acceptable level.
Cr(VI) is considered to be a genotoxic carcinogen when inhaled. A risk of 1 x 10^{-6} (one extra case of lung cancer per million persons) was calculated for lifelong exposure by inhalation to 0.025 ng Cr(VI).m^{-3} of air. This corresponds roughly to a risk of 10^{-8} per year, which, in accordance with the risk philosophy of the current standardization policy in the Netherlands, is considered to be negligible. According to the same policy philosophy, the maximum permissible level is a factor of 100 higher [2.5 ng Cr(VI).m^{-3}]. The ambient air Cr(VI) levels to which the Dutch population is exposed are not known; the current analytical methods are inadequate for determining the speciation of chromium in air. Estimates of the Cr(VI) fraction in ambient air range from 0.01 to 30%. Based on these data it cannot be excluded that nationally the Cr(VI) concentrations exceed the negligible risk level; it is conceivable that in the vicinity of Cr(VI)-emitting sources, the population is exposed to levels which are higher than the maximum permissible concentration. Therefore, in the workplace the risks of chromium cannot be neglected. However, in view of the autonomous developments, leading to a reduction in Cr(VI) emissions, it can be expected that locally the Cr(VI) concentrations will fall to below the maximum permissible level within a period of ten years.

With regard to the aquatic environment, a provisional maximum permissible concentration of 7 $\mu g.l^{-1}$ dissolved Cr [Cr(III) plus Cr(VI)] was derived for both fresh and sea water. This is the concentration at which, theoretically, 95% of the species present are protected, and which corresponds roughly to the current basic quality. As stated previously, this level is not, or no longer, exceeded. Adverse effects on aquatic organisms present in both fresh and sea water are not expected except where chromium is occasionally discharged. The natural background concentration is proposed as the desirable level: 1 $\mu g.l^{-1}$ for fresh surface water and 0.5 $\mu g.l^{-1}$ for sea water.
It is not as yet possible to calculate a corresponding reliable value for sediments on the basis of adsorption coefficients (K_d values); this matter is still under discussion.

There are insufficient ecotoxicological data on soil for establishing a scientifically underpinned recommended value. However, soil concentrations up to 100-200 $mg.kg^{-1}$ [total Cr, dry weight (level depending on soil characteristics such as % clay] (particle size < 2 μm)) do not appear to result in irreversible effects, or to pose problems for public health. This level corresponds roughly to the current reference value for soil.
For groundwater, the same recommended value as for surface water (7 $\mu g.l^{-1}$ dissolved Cr) is in principle proposed as the maximum acceptable concentration. Here, too, the natural background level is adopted as the desirable value, corresponding to the current reference value (1 $\mu g.l^{-1}$).
The chromium concentrations in Dutch soils are generally below the concentration range above which ecotoxic effects can be expected: about 10-120 $mg.kg^{-1}$. Only in water meadows and polders covered with harbour sludge higher levels (approximately 100-500 $mg.kg^{-1}$) are sometimes observed, and ecotoxic effects cannot be excluded here. Groundwater usually contains less than 1 $\mu g.l^{-1}$, and never exceeds the recommended level of 7 $\mu g.l^{-1}$. Because of chromium input to the soil, its chromium level will increase, but this accumulation is very limited. The reverse will be true for water meadows: because of input and sedimentation of sludge containing less chromium, the soil chromium level will fall in the longer term.

Although the data required for an adequate risk assessment are insufficient, it is concluded that the chromium-related risks to man and the environment will be limited, both at present and in the future. In view of the autonomous developments, which are expected to lead to a reduction in emissions, and thereby exposure levels, the risks will decrease still further. Feasible additional measures are limited and are aimed especially at chromium reuse and chromium-containing waste reduction in the leather industry. Nevertheless, because of the uncertainties regarding exposure to chromium by inhalation, further research is advisable into (a) an adequate analytical method for determining the Cr(VI) fraction, (b) the establishment of a (possible) relationship between Cr(VI) sources and the presence of Cr(VI) in outdoor air, and (c) the establishment of a (possible) relationship between concentrations of photo-oxidants and Cr(VI), because oxidants can retard the conversion of airborne Cr(VI) to Cr(III).

INTRODUCTION

Environmental policy at government level is first of all aimed at attaining and maintaining an environmental quality which ensures the general health and wellbeing of man and the preservation of animals, plants and goods (Indicative Multi-year Programme - Environmental Management 1986-1990). However, with insufficient knowledge it is impossible for the time being to describe fully the overall environmental quality in view. Attention is therefore being focussed on factors which probably entail considerable risks, including environmentally harmful substances. A selection has been made of the many substances of relevance, because of emission or use, and a priority list compiled. In principle, so-called integrated criteria documents are drawn up for most of the priority substances.

Integrated criteria documents contain, per substance or substance group, data on the sources and the distribution pattern (soil, water, air, biota), the risks of actual exposure concentrations and the exposure expected for man, (parts of) ecosystems and materials, and the technical possibilities and financial consequences for the industries concerned of reducing these risks. This information serves as the scientific basis for formulating the effect-oriented environmental policy. This policy is aimed at attaining as large a risk reduction as possible, the desirable level being the ultimate goal. This value is the concentration in the environment at which no adverse effects occur for man, plants, animals and materials (effects of which the risk is considered to be negligible). If the desirable level cannot be reached within a reasonable period of time, a limit value is established for a limited period, with the risks lying between the maximum permissible and the desirable concentrations. In addition to the possible risk reduction, economic and social factors are also determinants in setting this limit value. This document is confined to the provision of information necessary for the establishment of the above-mentioned environmental quality criteria in terms of policy; the information supplied may also result in a general task-setting for the emission reductions per source. The sections of this document do not, therefore, contain a policy opinion.

The National Institute of Public Health and Environmental Protection (RIVM) is responsible for drawing up integrated criteria documents. The firms

Haskoning and DHV, consulting engineers, participated in the realization of this report, while the Institute for Environmental Issues (IvM) also made a contribution. Government, business and industry, environmental groups and representatives from scientific institutes were involved in the preparation of this report (including the exploratory meeting, the hearing prior to the drafting of the working document, and sources of information). The document has been checked in its entirety by a Review Committee of the RIVM, while an Advisory Board composed of staff from the Ministry of Housing, Physical Planning and the Environment, the Department of Inland Waterways/National Institute for Wastewater Research (DBW/RIZA) and the Ministry of Agriculture and Fisheries gave guidance in its compilation. Business and industry supplied important, partly confidential, information through the ad hoc Working Group on Integrated Criteria Documents of the Office of Environment and Physical Planning of the Council of Dutch Employers' Unions, VNO and NCW. In case of differences of opinion, an addendum drawn up by the ad hoc Working Group may be added to the document. This possibility also exists for environmental groups through the Nature and Environment Foundation (Stichting Natuur en Milieu). At a later stage the Health Council will publish a brief report on the document, including any addenda.

This document deals with the heavy metal chromium; integrated criteria documents on cadmium and copper have previously been published. In view of the problems and the gaps in knowledge, the emphasis in this document will be mainly on the sources and emissions, forms of occurrence and accumulation, behaviour in soil and surface water, behaviour and occurrence in air, and chromium toxicity. In compliance with the wishes of the commissioning body, the sections concerning effects are based as far as possible on existing recent reviews. The original literature was only consulted when the review papers contained inconsistent data or conclusions. However, the original literature was used as a basis for deriving a toxicological recommended value. In addition, articles of a more recent date than the consulted reviews were evaluated.

1. PROPERTIES AND EXISTING STANDARDS

1.1. PROPERTIES

1.1.1. Forms of occurrence

Chromium (symbol Cr, atomic number 24, atomic weight 52.00) does not occur in the free state in nature, but in double oxides, principally as chromite ($FeO.Cr_2O_3$) and, to a lesser extent, as crocoite ($PbO.CrO_3$). The black mineral chromite is used almost exclusively for the production of chromium, its Cr_2O_3 content varying from 40 to 55%. The Cr^{3+} can be partly replaced by Al^{3+}. The average chromium concentration in the earth's crust is about 100 mg.kg (Krauskopf, 1979). Four natural isotopes are known: $^{50}_{24}Cr$ (4.35%), $^{52}_{24}Cr$ (83.79%), $^{53}_{24}Cr$ (9.59%) and $^{54}_{24}Cr$ (2.36%) (Holleman and Wiberg, 1985). Chromium is found in the environment nearly always in Cr(III) and Cr(VI) compounds, with the dominating Cr(III) in the $Cr(OH)_n^{(3-n)+}$ form and Cr(VI) always in the CrO_4^{2-} or $HCrO_4^-$ form. Cr(III) and Cr(VI) can be interconverted, depending on the conditions (see 3.1.).

In an important industrial manufacturing process of chromium, the Cr(III) in chromite is first converted into Cr(VI) at about 1100 ^{o}C with oxygen. The principal industrial chromium compound is sodium dichromate, which is the starting material for the production of nearly all other chromium compounds.

Chromium is the chief alloying metal for the manufacture of various types of noncorroding heat-resisting steel. A chromium content of up to 6% increases the hardness of the steel used for steam boilers and heating appliances, while above 10% it makes steel resistant to acids and oxidation at high temperatures ("rustproof"), and suitable for instruments, washing machines, etc. Well-known alloys are ferrochromium (Fe/Cr $\simeq$ 40/60), Cr/Co-, Cr/Si- and Cr/Ni-steel. The last-mentioned alloy is used in resistors and thermocouples, and in all kinds of piping, sheet and profile materials.

1.1.2. CAS registration numbers

chromium	7440-47-3
chromium(III) acetylacetonate	21679-31-2
chromium(II) chloride	10049-05-5
chromium(III) chloride	10025-73-7
chromium(III) chloride.$6H_2O$	10060-12-5
chromium(III) hexacarbonyl	13007-92-6
chromium(III) nitrate.$9H_2O$	7789-02-8
chromium(III) oxide	1308-38-9
chromium(VI) oxide	1333-82-0
chromium(III) sulphide	12018-22-3
cobalt chromium molybdenum	12629-02-6
chromium molybdenum steel	12676-02-7
potassium chromate	7789-00-6
potassium dichromate	7778-50-9
lead chromate	7758-97-6
copper chromite	12053-18-8
sodium dichromate.$2H_2O$	7789-12-0
sodium chromate.$4H_2O$	10034-82-9
chromium potassium sulphate.$12H_2O$	7788-99-0
chromyl chloride	14977-61-8

1.1.3. Physical properties

Chromium is a silvery brittle metal with a density of 7.14 g.cm^3. The most striking physical properties of chromium are its great hardness, its brilliant resistant metallic lustre, its high wear and abrasion resistance, and its high melting point (over 1900 °C. The boiling point is around 2640 °C.

A number of physical properties of chromium compounds which are environment-relevant or have been used in experiments are given in table 1.1. It should be noted that a number of chromium salts can exist in both a soluble and an insoluble form.

1.1.4. Chemical properties

Chromium belongs to the group of VIA elements in the periodic table together with molybdenum and tungsten. These metals all exhibit a certain degree of "noble" behaviour, which characterizes their corrosion resistance. Chromium belongs to the transition metals, the electron configuration of the outer electrons being $4s3d^5$. Consequently, it has a complex chemistry: compounds of all oxidation states from +6 to -2 are known, but only +6 or +3 are detected in the environment.

There are thousands of Cr(III) compounds, which show a wide range of colours. In the Cr(III) form, the electron configuration (d^3) is ideal for the formation of octahedral structures, which give the Cr(III) compounds an exceptionally great stability. The chemistry of Cr(III) resembles that of aluminium: Cr_2O_3 is amphoteric, albeit more basic than acid.

In oxidation state +6, chromium becomes acidic: it is then a powerful oxidizing agent. Cr(VI) only exists in combination with oxygen in compounds such as chromates. CrO_3 is the anhydride of chromic acid which is widely used as an oxidizing agent. However, its salts are in this respect, in a basic environment, less powerful than the permanganates. Dichromate solutions passivate metal surfaces, and are therefore frequently used as corrosion inhibitors.

The behaviour of chromium in acids depends on its pretreatment. When chromium has been immersed in a powerful oxidizing acid, such as nitric or chromic acid, it becomes passive and thereafter no longer dissolves in dilute acids, but when dipped in a reducing solution, it becomes active and does dissolve in dilute acids. At elevated temperatures, chromium reacts with most non-metals, such as O, S, N, C, Cl, B, Si.

Table 1.1. *Melting point, boiling point and solubility in water of a number of chromium compounds (TDB, 1985; Weast, 1975)*

Compound	*Formula*	*Melting point ($^{\circ}$C)*	*Boiling point ($^{\circ}$C)*	*Solubility (g per 100 ml)*
Chromium(III)chloride	$CrCl_3$	1150	1300	sparingly sol.
Chromium(III)oxide	Cr_2O_3	2435	4000	5.10^{-5}
Chromium(III)orthophosphate	$CrPO_4.6H_2O$	100	-	sparingly sol.
Chromium(III)hydroxide	$Cr(OH)_3$	-	-	5.10^{-4} (pH=5)
Chromium(III)nitrate	$Cr(NO_3)_2.9H_2O$	357	100	soluble
Chromium(III)sulphate	$Cr(SO_4)_3$	-	-	insoluble
Chromium(III)sulphate.hydr.	$Cr_2(SO_4)_3.18H_2O$	100	-	100
Chromium(VI)oxide	CrO_3	196	decomp.	61.7
Ammonium chromate	$(NH_4)_2CrO_4$	180	-	40.5
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	170	-	30.8
Barium chromate	$BaCrO_4$	-	-	$4.4.10^{-3}$
Calcium chromate	$CaCrO_4$	-	-	16.3
Potassium chromate	K_2CrO_4	968	-	63
Potassium dichromate	$K_2Cr_2O_7$	398	500(decomp.)	4.9
Mercury(I) chromate	Hg_2CrO_4	-	decomp.	sparingly sol.
Lead chromate	$PbCrO_4$	844	decomp.	insoluble
Sodium chromate	Na_2CrO_4	20	-	>40
Sodium dichromate	$Na_2Cr_2O_7.2H_2O$	357	400(decomp.)	238
Zinc chromate	$ZnCrO_4$	-	-	sparingly sol.

1.2. EXISTING STANDARDS AND GUIDELINES

1.2.1. Soil and groundwater

The reference values for chromium in soil and groundwater given in the Environmental Programme 1988-1991 (MPV88, 1987) are 50+2C $mg.kg^{-1}$ dry weight and 1 $\mu g.l^{-1}$ respectively, where C is percent clay (diameter < 2μm) by weight. For a standard soil with a clay content of 25%, the reference value is thus 100 $mg.kg^{-1}$ dry weight. At this or lower chromium concentrations the soil is considered to be multifunctional, that is, chromium is not expected to cause adverse effects. When assessing the soil quality, the technical manual still to be published must be used. A test framework for the assessment of the concentration values in soil has been given in the draft Soil Cleanup Guide (VROM, 1987) (table 1.2.). The indicative guidelines mentioned in this guide should not be regarded as standards but as an assessment framework.

Table 1.2. Test framework for the assessment of the concentration values of chromium in soil (VROM, 1987)

	A	B	C
Soil (mg per kg dry weight)	*50+2C*	*250*	*800*
Groundwater (μg per litre)	*1*	*50*	*200*

C = clay content (diameter< 2 μm)
A = reference value, 100 mg.kg^{-1} dry weight for a standard soil, equal to MPV88 value
B = test value for the purpose of further research
C = test value for the purpose of cleanup research

For the use of cleaned soil, without restrictions, the draft working paper " Establishment of Standards for Use of Cleaned Soil" (DGM, 1988) assumes the same A value.

The EEC (1980a) has issued a directive for the protection of groundwater, making it obligatory for the member states to limit contamination by list II substances (including chromium) in groundwater.

Sewage sludge, compost and organic soil

At present, the Fertilizers Act regulates the quality of animal manure and other organic fertilizers and the Soil Protection Act controls their use. According to the "Draft Decree on Quality of other Organic Fertilizers" (draft 27 October 1988), there will be a phased tightening of the standards for sewage sludge, compost and organic soil in the years to come (table 1.3.).

Table 1.3. Standards for chromium with respect to the quality of other organic fertilizers (mg.kg^{-1} dry matter)

Organic Fertilizer	*Period* *up to 1/1/91*	 *1/1/91 - 1/1/95*	 *1/1/95 - ca 2000*
Sewage sludge	*500*	*350*	*ca 75*
Compost	*300*	*200*	*ca 60*
Organic soil	*50 + 2C*		

Application of sewage sludge or compost is only permitted when (mandatory) soil research has shown that the reference values for heavy metals and arsenic have not been exceeded. An exception to this rule is the use of "clean" compost from plant waste, which is regarded as reuse, for which soil research is not mandatory. The standards for the use of sewage sludge, compost and organic soil are listed in table 1.4.

Table 1.4. Standards for the use of other organic fertilizers (tonnes of dry matter/ha)

Land use	Sewage sludge		Compost			Organic soil
	liquid	firm	from sludge	from mixed wastes	from plant waste	
Grassland	1 tonne/yr	prohib.	prohib.	prohib.	unlimited	unlimited
Agricultural soil and maize soil	2 tonnes/ year	4 tonnes/ 2 years	4 tonnes/ 2 years	12 tonnes/ 4 years	unlimited	unlimited
Natural terrain	prohib.	prohib.	prohib.	prohib.	unlimited	unlimited
Other soil	prohib.	prohib.	4 tonnes/ 2 years	12 tonnes/ 4 years	unlimited	unlimited

The problem is being further worked out and definitive regulation, with the possibility of considerable modifications, is expected early in 1990.

In the EEC context, several countries and the EEC have made proposals with respect to agricultural soil for limit values for the chromium content of soil and sludge, and for the maximum permissible annual chromium input to the soil via sludge (table 1.5.). The EEC (1988a) assumes provisionally (now under discussion) a total Cr(III) input to the soil of 300-600 kg.ha^{-1}, which amounts to an annual permissible input of 10 kg.ha^{-1}.

Table 1.5. Proposals with respect to agricultural soil for maximum concentrations in soil and sludge (mg.kg^{-1}), and the annual permissible chromium input to the soil (kg per ha per year; EEC, 1988a)

Country	*Soil*	*Sludge*	*Soil input*
The Netherlands	*100-250*	*500*	*1*
Belgium	*150-250*	*500*	*2*
Germany	*100-150*	*1000-1200*	*2-3*
France	*150-250*	*1500-2500*	*10*
Italy	*100-150*	*750-1000*	*3-4*
EEC	*150-250*	*1500-2500*	*10*

1.2.2. Water and sediments

The Netherlands

The maximum permissible level of chromium in surface water intended for the production of drinking water is 50 $\mu g.l^{-1}$ (Staatsblad 606, 1983). The chromium concentration in shellfish water should not be so high that shellfish and their larvae are adversely affected (Staatsblad 606, 1983); however, a concentration is not given.

In the IMP Water 1985-1989 (1984) the basic quality for surface water is 50 $\mu g.l^{-1}$ chromium (total). The guidelines of the Association of Water Boards of 1974 are used for the treatment of effluents.

For the Cr concentration in sediments, the initial impetus has recently been given to establish recommended standards, with the assumption that the general environmental quality of sediments and the reference value for soil quality indicate in principle an identical protection level. The maximum permissible Cr content for the general environmental quality of the sediments is 100 $mg.kg^{-1}$. The provisional C value, the value above which research into the need for cleanup is urgent, has been set at 600 $mg.kg^{-1}$. This discussion is still under way. For example, DBW/RIZA (1989) has derived an ecotoxicological value for surface water of 2.5 and 24 $\mu g.l^{-1}$ (dissolved and total Cr, respectively), and 725 and 483 $mg.kg^{-1}$ for the suspended materials and the sediments, respectively. In addition, DGM/RIVM is preparing a working paper.

International

Chromium has been included as a grey-list substance in the EEC directive 76/464/EEC of 4 May 1976 (EEC, 1982). The policy for grey-list substances is aimed at reducing emissions using the best feasible techniques. The maximum permissible concentration in surface water intended for the production of drinking water is 50 $\mu g.l^{-1}$ chromium (total) (EEC, 1975). The quality of shellfish water should be such that the chromium concentration in the soft tissue of shellfish is so low that it contributes to a good quality of shellfish products (EEC, 1979). The Council of the European Communities (EEC, 1988b) has proposed quality objectives which must be implemented as of 15 September 1991 (table 1.6.). The proposed emission standard for the discharge of total chromium from industrial activities from that date is 2 $mg.l^{-1}$ of discharged waste water.

The international association of water companies along the Rhine (IAWR, 1986) prescribes that the Cr concentration in the River Rhine should not exceed 50 $\mu g.l^{-1}$ when drinking water is produced by a physicochemical procedure, and 20 $\mu g.l^{-1}$ when only natural purification methods are used.

Table 1.6. EEC quality objectives for 15 September 1991 concerning the annual average Cr concentration ($\mu g.l^{-1}$) in surface water (EEC, 1988b)

Environmental compartment	*Water of high ecological value*	*Water of lesser ecological value*	*Specification*
*Inland surface water**	*10*	*20*	*total Cr*
Estuaries	*5*	*10*	*total Cr*
Coastal waters except estuaries	*3*	*3*	*dissolved Cr*
Territorial waters	*3*	*3*	*dissolved Cr*

** for water with an average hardness of 100 $mg.l^{-1}$ as $CaCO_3$; for softer water stricter objectives must be established*

1.2.3. Air

Tables 1.7. and 1.8. list the quality criteria in the workplace and for ambient air, respectively.

Germany has set emission limits for Cr(VI) compounds, insofar as chromates of Ca, Cr(III), Sr and Zn are concerned. With a mass flow greater than 5 $g.hour^{-1}$, the maximum permissible emission concentration is 1 mg $Cr.m^{-3}$, and continuous measurement of the emission concentration is required when the mass flow exceeds 25 $g.hour^{-1}$. For chromium and Cr compounds (as Cr), the maximum permissible emission concentration is 5 $mg.m^{-3}$ when the mass flow exceeds 25 $g.hour^{-1}$. Continuous measurement of the emission concentration is required with a mass flow greater than 125 $g.hour^{-1}$ (TA-Luft, 1986).

Several organizations in America (NIOSH, OSHA and ACGIH) have proposed various standards for the workplace (table 1.7.).

Table 1.7. *Air quality criteria in the workplace (MAC values, time-weighted average, TWA, for an 8-hour day, 40-hour workweek),* $\mu g.m^{-3}$

Country	MAC value	Comment	Reference
The Netherlands	50	chromates (a few water-insoluble salts)	National MAC list (1986)
	150	chromyl chloride, alteration planned	
	500	chromium and water-soluble salts (as Cr) (MAC value under consideration)	
	50	chromic acid and chromates (as Cr)	
	500	metallic Cr	WGD (1985)
	25	Cr(VI) compounds, soluble	
	50	as above, TWA-15 minutes	
	500	Cr(III) compounds	
	1000	as above, TWA-15 minutes	
	10	chromates of Ca, Sr and Zn, TWA-15 minutes	
	25	Chromates of Pb and Ba, TWA-15 minutes	
West Germany	100	CrO3	Leegwater et al. (1984)
US	500	chromium metal	EPA (1984)
	500	Cr(II) compounds (as Cr)	
	500	Cr(III) compounds (as Cr)	
	50	Cr(VI) compounds (as Cr), water-soluble	
	50	Cr(VI) compounds (as Cr), water-insoluble	
US, NIOSH	50	CrO_3, TWA	
	100	maximum	
	1	Cr(VI), carcinogenic	
	25	Cr(VI), non-carcinogenic	
US (proposal)	25	non-carcinogenic chromium(VI)*	
	50	(maximum)	
	1	carcinogenic chromium(VI)**	
	50	chromic acid (as chromium trioxide)	
	100	(maximum)	
	500	soluble chromium or chromium salt	
	1000	insoluble salts or chromium metal	
	500	chromium metal	
	500	chromium(II) compounds	
	500	chromium(III) compounds	
	50	chromium(VI) compounds-soluble	
	50	-insoluble	
	50	chromium ore	
	500	soluble chromium and chromium salts	

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* by non-carcinogenic Cr compounds NIOSH understands the mono- and dichromates of hydrogen, lithium, potassium, rubidium, caesium, ammonium, and chromium oxide (chromic anhydride)

** by carcinogenic Cr(VI) compounds NIOSH understands all Cr(VI) compounds except the Cr(VI) compounds in footnote *

Table 1.8. Ambient air quality criteria ($\mu g.m^{-3}$; IDC, 1985)

Country/province	*Concentration*	*Comment*
USSR	*1.5*	*daily average; Cr(VI) (as CrO_3)*
	1.5	*maximum conc. for up to 20 minutes*
East Germany	*1*	*daily average*
	1.5	*30-minute average*
Israel	*1.5*	*daily average; not to be exceeded for more than 3 days per year; Cr(VI) (as CrO_3)*
China	*1.5*	*maximum; Cr(VI)*

International

At a concentration of 1 $\mu g.m^{-3}$ Cr(VI) in ambient air the WHO has estimated the risk of lung cancer at 4.10^{-2} for lifelong exposure (WHO, 1987).

1.2.4. Food and drinking water

In the EEC context, there is the regulation that colouring agents for use in food are not permitted to contain more than 100 $mg.kg^{-1}$ chromium sulphate. When sulphates of antimony, copper, zinc or barium are also present, the total of the concentrations of the substances mentioned should not exceed 200 $mg.kg^{-1}$ (IRPTC, 1978). Furthermore, estimates have been made in the foreign literature of the desirable daily chromium intake. This is dependent on age (table 1.9.).

Table 1.9. Proposed daily dietary intake of chromium (mg; NAS, 1980)

Age	*Amount*
< 0.5 year	*0.01-0.04*
0.5-1 year	*0.02-0.06*
1 -3 years	*0.02-0.08*
4 -6 years	*0.03-0.12*
7 -10 years	*0.05-0.2*
>11 years	*0.05-0.2*
adults	*0.05-0.2*

The drinking-water standards are summarized in table 1.10.

Table 1.10. *Drinking-water standards ($\mu g.l^{-1}$; Cr(VI))*

Country	*Standard*	*Reference*
The Netherlands	*50*	*Water Board Decree (1984)*
Germany	*50*	*SCMO/TNO (1977)*
EEC	*50*	*EEC (1980b)*
US	*50*	*EPA (1984)*
USSR	*100*	*Zielhuis (1981)*

1.2.5. Other

According to the Cosmetics Decree (Food and Drugs Act, 1980), cosmetics should not contain chromium salts and chromic acid or its salts.

The Chemical Waste Act (Staatsblad 435, 1977) defines Cr(VI) and Cr(III) compounds as chemical waste when the concentrations exceed 50 and 5000 $mg.kg^{-1}$ dry weight, respectively.

2. PRODUCTION, APPLICATIONS, SOURCES AND EMISSIONS

This chapter outlines the production, applications, sources and emissions of metallic chromium, chromium compounds and other chromium-containing substances. The method used is represented in figure 2.1. Separate chromium flows in the economy and in the environment form the basis, where chromium can enter the environment via emissions from the economy. These emissions can be classified by type of environmental compartment: air, soil and water. An detailed description has been given in the background report drawn up by Haskoning (1988).

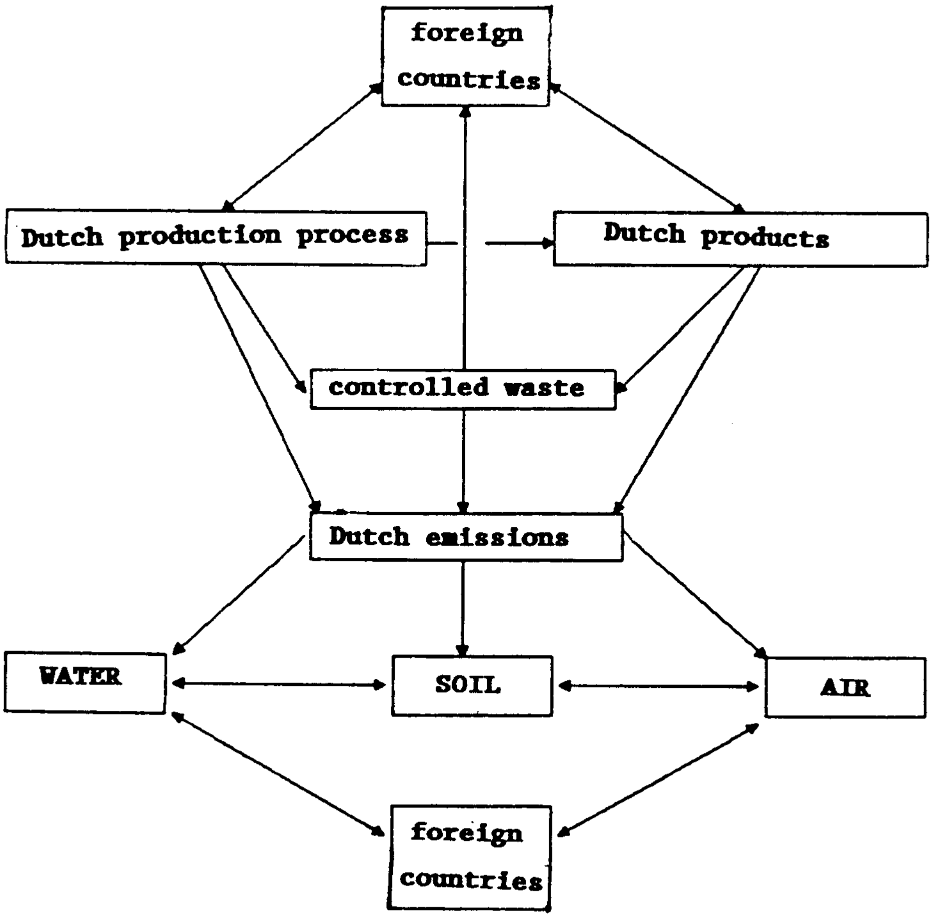


Figure 2.1. Schematic representation of material flow (adapted from Udo de Haes et al., 1988; CBS, 1988a)

2.1. PRODUCTION AND APPLICATIONS

2.1.1. Production processes

Chromium and chromium products are produced chiefly from chromite ore (not in the Netherlands). Ferrochromium is produced from chromite by reduction, and serves as the raw material for the production of chromium alloys. Treatment of chromite with sodium carbonate gives sodium dichromate, which serves as the starting material for a large number of chromium compounds (Kirk & Othmer, 1978; Hartford, 1979; IARC, 1980; IRPTC, 1987).

2.1.2. Trade volume

World production of chromite ore in 1986 was over 10,000 ktonnes. The largest chromite producers in Western Europe were Finland and Greece (World Bureau of Metal Statistics, 1987). Chromite ore is not mined in the Netherlands.

The Dutch balance of trade for 1986 for metallic chromium, chromium compounds and other chromium-containing substances is given in Haskoning (1988). Alloys (stainless steel), chromium-plated articles (car parts, etc.), synthetic substances (pigments) and the like have here been disregarded, because the quantities of chromium involved are not known.

Cr(VI) compounds are included in the first priority substances list and its first draft revision (Priority Substances Regulation, art. 22 of the Environmentally Hazardous Substances Act). Companies are therefore under obligation to provide data on occurrence, application and distribution of the substances on this list.

According to the survey conducted recently by the Ministry of VROM, 1347 tonnes of Cr(VI) were imported in 1986, and 596 tonnes exported. This means a (calculated) net consumption in 1986 of 751 tonnes of Cr(VI) (VROM, 1988a).

2.1.3. Applications and consumption

The demand for chromium in 1981 was estimated to be about 32,500 tonnes in Western Europe and about 2,500 tonnes in the Netherlands (SRI, 1985). The industrial uses of chromium can be divided into three main categories: (a) metallurgical applications, (b) refractory applications, and (c) chemical applications. The distribution of chromium consumption in the Netherlands in 1986 over the three main categories is given in table 2.1., that of the quantities of chromium chemicals used per area of applications in table 2.2.

Table 2.1. Quantities of chromium (in tonnes) in 1986 per main category of applications

Application	chromium (0, III, IV)	chromium (VI)[4]
Metallurgical	52	0
Refractory	7[1]	0
Chromium chemicals	996	751

1) telephonic business information from refractory industry

Table 2.2. Quantities of chromium present in chromium chemicals consumed in the Netherlands in 1986 per area of applications

Application	Cr (0, III, IV)		Cr (VI)		Compound
	(tonnes)	(%)	(tonnes)	(%)	
Metal-surface treatment (chromium-plating, passivating, chromizing, pickling)	<3	0	173	23	chromium trioxide, sodium and potassium dichromate
Pigments (general)	21[1]	2	459	61	lead chromates, molybdate red/orange
Corrosion-resistant pigment/constituent, primer			23	3	zinc chromate, zinc tetroxychromate
Leather tanning agent	650[2]	65			chromium sulphate, chromium trioxide
Wood preservation			98	13	chromium trioxide
Magnetic tapes	325[3]	32			chromium dioxide
Cooling water			<1	<0.1	chromate
Other + unknown (e.g. photosensitization, ceramics)			<4	<0.5	ammonium dichromate, chromium trioxide, lead chromate
Total	±1000	100	±755	100	

1) tel. survey by VVVF ; 2) TNO (1985); tel. business inf. from leather industry; 3) tel. business inf. from magnetic tape industry; 4) from VROM (1988a)

2.2. SOURCES AND EMISSIONS

2.2.1. Production of chromium compounds

In 1986, the Netherlands produced about 4,500 tonnes of chromate pigments from (imported) raw materials (mainly sodium dichromate) (VROM, 1988a). Chromium(III) acetylacetonate (<100 tonnes in 1986) was made from imported chromium sulphate. The associated emissions were (in tonnes of chromium) (Haskoning, 1988):

Cr(VI) (pigment production):	
- surface water	0.3
- air	0.1
- chemical waste	12 (wastewater sludge, dust filters)
Cr(III) (chromium acetylacetonate production):	
- waste water	<0.1
- air	<0.01

The pigment suppliers expect a moderate to sharp drop in sales of chromate-containing pigments (VROM, 1988a; TNO, 1987). In addition, as a result of the policy for reducing lead, a shift can be observed from lead chromates to chromium-free pigments (VVVF, pers. comm.).

2.2.2. Applications

- Metal products industry

Chromium is used in the metal products industry in several metal-finishing operations. Metal-surface treatments which may generate Cr emissions can be divided into (chromic acid) anodizing, electroplating (chromium plating), chromizing, passivating, pickling, as well as blasting and de-varnishing. According to the Ministry of VROM (VROM, 1988a), about 162 tonnes of Cr(VI) are used annually, of which 93% for chromium plating and 7% for passivating and chromizing.

The RIVM (1985b) reported that the electroplating industry currently still discharges annually 9.9 tonnes of Cr(III) into surface waters.

Gas bubbles emanate from the chromic acid baths during chromium plating. These gas bubbles introduce Cr(VI) into the air of the workplace. Estimated emissions per square metre of bath surface area are about 14 g per hour during "hard" chromium plating. The emission factor for "decorative" chromium plating is about 60% lower (State of California, 1986). Telephonic business information revealed that a large chromium consumer emits annually less than 10 kg of chromium into the air after installation of a chromic acid collecting device. This means that, if it is assumed that all electroplating plants have installed a chromic acid collector, Cr(VI) emission into the air is an estimated 0.2-0.4 tonne per year. The Ministry of VROM (VROM, 1988b) calculated that the atmospheric emission of chromium is less than 3 tonnes annually.

It is believed that approximately 300 electroplating companies process chromium, generating an annual waste stream of 1,500 tonnes of electroplating sludge (d.w.). This electroplating sludge contains about 20,000 μg Cr(III).g^{-1}, which amounts to an estimated chromium load of 30 tonnes per year (RIVM/LAE, pers. comm.). At present, this sludge is transported to other countries.

- Paint industry

Chromium-containing pigments are used extensively in the paint industry. These pigments can be subdivided into pigments based on chromates (for example, lead chromates and molybdate red), pigments based on chromium(III) oxide green, and corrosion-inhibiting pigments based on zinc chromate (zinc yellow) and zinc tetroxychromate.

- Production

In the manufacture of paint, 1-2% ends up in industrial waste, which amounted to 0.1-0.2 tonne of Cr(III) and 2-4 tonnes of Cr(VI) in 1986; chromium emissions into air and surface water are normally negligible (Haskoning, 1988).

- Application

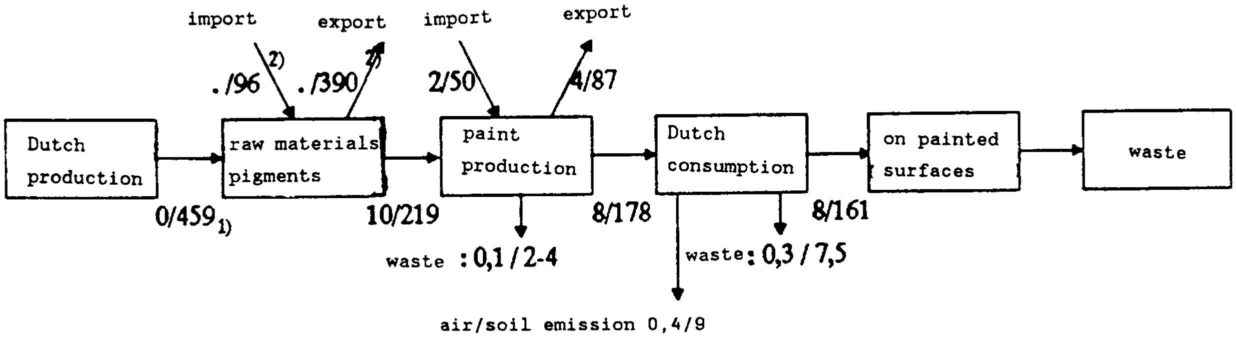
As a result of spray painting in the open air and in rooms without exhaust with paint-collecting equipment, a considerable amount of paint is lost to the environment. On the basis of data from the VVVF and the RIVM, the quantities of chromium which end up in waste streams or are emitted into air and soil (diffuse) have been calculated (assuming that 5% of the overspray remains in the air for some time before being deposited) (Haskoning, 1988), see table 2.3.

Table 2.3. Chromium emissions in the Netherlands in 1986 from paint application

	Cr(III) (tonnes)	*Cr(VI) (tonnes)*
Soil	*0.4*	*8.5*
Air	*<0.05*	*0.5*
Waste water	*0*	*≥0.2**
Waste	*0.3*	*7.5*

**) 0.2 tonne from paint use by private individuals; amount from industrial use is not known*

A flow diagram for chromium relating to the production and use of paint products in the Netherlands in 1986 is given in figure 2.2.; it should be noted that the balance does not tally arithmetically, because data from several sources have been used.



[1]) from VROM (1988a) (61% of the total Dutch production)

[2]) from CBS (1986) (average chromium content pigments stated 10%)

Figure 2.2. Flow diagram of chromium relating to the production and use of paint in the Netherlands in 1986 (in tonnes of Cr(III)/Cr(VI))

There is a trend in the paint industry to replace chromate pigments [Cr(VI)] with other pigments. However, market acceptation of more environmentally acceptable, corrosion-resistant paints is still limited. The pigments used because of their colour (chromium yellow, chrome green and molybdate orange/red) can, with the present state of technology, be replaced only in certain cases with other organic pigments.
The use of Cr(III)-containing pigments has decreased by about 90% in the past few years as a result of a change in the quality criteria of camouflage paint, by far the major use for these pigments (pers. comm. VVVF).

- <u>Base metal industry</u>

The Dutch base metal industry does not refine chromite. However, imported ferrochromium is added to iron on a limited scale (mostly small iron foundries) to obtain certain steel alloys (tel. business inf.). In addition, chromium-containing ferrophosphorus, a by-product of the phosphate ore-processing industry, is used in certain production processes (see also phosphate ore-processing industry).
According to the emission registration of the Ministry of VROM (VROM, 1988b) Cr(III) emission into the atmosphere was about 1.5-2 tonnes per year (1978-1983 data). In 1984-1985 the largest emitter of all installed a dust exhaust system. The current emission (1986) into air is estimated to be about 1 tonne per year (tel. business inf.). This industrial sector discharged 1.4 tonnes of (probably) Cr(III) into surface water in 1985 (IMP Water 1985-1989).

- <u>Leather, shoe and other leatherware industries</u>

The use of chromium chemicals in the leather industry is based on the power of Cr(III) to form stable complexes with celluloses, dyes, proteins and various synthetic polymers. In the Netherlands so-called chrome tanning of leather takes place at about 5 companies. In addition, beamhouse operations are carried out on a limited scale at four companies. About 21 leather plants process only "wetblue" (wet-chrome-tanned) cattlehides and have no beamhouse operations and therefore no beamhouse waste streams (TNO, 1985; VROM, 1988c).
About 650 tonnes of Cr(III) are consumed annually in the leather, shoe and other leatherware industries in the Netherlands (TNO, 1985). Since the production of the Dutch leather industry is estimated to be 20,000 tonnes

of hides and these hides contain 2-3% chromium after treatment, it is assumed that 400-600 tonnes of chromium are incorporated in the product (VROM, 1988c).

Dutch leather consumption by private individuals is, converted to chromium, about 250 tonnes per year (according to information from Centre Economique du Cuir, and tel. business inf.). Part of this will eventually end up in urban waste.

Chromium input to surface water in 1985 was estimated to be 2.5 tonnes (IMP Water 1985-1989; CBS, 1988a). Emissions into the atmosphere are negligible.

The province of North Brabant has catalogued the waste streams from the leather industry by visiting companies and conducting surveys. The estimated quantities of chromium-containing waste streams from the Dutch leather plants which manufacture chrome-tanned leather are given in table 2.4., as well as the chromium-containing waste stream from the shoe and other leatherware industries. The province of North Brabant reported that 2300 tonnes (ca 30%) of the combined shavings, clippings and remnants are directly exported, and subsequently upgraded and processed. A large part of the remaining 5200 tonnes is indirectly transported to other countries. The rest is only allowed to be deposited in the dump "De Spinder" near Tilburg, together with the sludge. As of April 1987, reuse of shavings in riding academies is no longer permitted (VROM, 1988c).

Table 2.4. Chromium-containing waste from the Dutch leather industry in 1986 (province of North Brabant, 1988)

Waste type	*Cr(III) content (%)*	*Water content*) (%)*	*Amount (tonnes/yr)*	*Chromium (tonnes/yr)*
Shavings and clippings	*3*	*60*	*2,870*	*34*
Remnants	*3*	*60*	*3,258*	*39*
Sludge	*2*	*60*	*4,630*	*36*
Total			*10,758*	*110*

**) from TNO, 1985*

- Printing industry

The printing industry uses chromium in intaglio and certain offset techniques. In offset, a printing plate is used consisting of a base of metal (aluminium), plastic or paper to which a photosensitive layer of photopolymers, diazo compounds or bichromates has been applied. On the copying layer of the presensitized aluminium plates is a microns-thin copper or brass and chromium layer. After exposure, the plates are developed and fixed with alkaline and acid solutions or mixtures of organic solvents (Stichting Natuur & Milieu, 1986). A few large firms use plates consisting of copper, chromium and a bichromate-containing copying layer. After developing the plates, the chromium layer is etched in an acid zinc chloride solution. In intaglio, the plate cylinder is hard chromium plated to make the surface more resistant to wear (Stichting Natuur & Milieu, 1986).

The total discharge of chromium into surface water by the printing industry is estimated at 1.1-1.2 tonnes per year (RIVM, 1985b; IMP Water 1985-1989). It can be deduced from the emission registration of the Ministry of VROM (VROM, 1988b) that about half is emitted as Cr(VI) and that intaglio accounts for by far the greater part of the discharge. Chromium emissions into the air are negligible (VROM, 1988b). It can be expected that emissions from the intaglio establishments will decrease, because the water-quality managers will set the same criteria as for the electroplating plants.

- <u>Textile industry</u>

At present, chromate is still used in a few cases as a mordant to fix certain dyes. In addition, chromium chelates are used to dye wool and nylon fibres. The Dutch textile industry discharged 1.1 tonnes of Cr(III) into surface water in 1985. Atmospheric emissions are negligible (VROM, 1988b).

- <u>Wood-impregnating industry</u>

Haskoning (1988) describes in great detail the impregnating and fixing processes and the possible emissions involved, and the emissions from the storage of the impregnated wood. On the basis of Broers & Partners (1988), NEHEM (1986), TNO (1987) and DBW/RIZA (pers. comm.), Haskoning gives the following figures for 1986:

volume of treated wood	ca	170,000 m^3
chromium(VI) consumption in impregnating salts (109-272)		120 tonnes
emissions as a result of impregnating and fixing	ca	0 tonne
emissions into soil as a result of storage (part of this can enter surface water or municipal sewage via a paved yard provided	ca	0.2 tonne

with a sewer system (Tebodin, 1984).

Figure 2.3. gives an idea of the mass balance for chromium present in impregnating salts. Of the approximately 167,000 m^3 of impregnated wood, 11,400-33,000 m^3 (Haskoning, 1988 and DBW/RIZA, pers. comm.) is used annually in hydraulic engineering. The emissions from leaching relating to the applications are discussed in section 2.2.4. under "Diffuse sources". The impregnated wood must be processed in the waste stage as chemical waste. The useful life of impregnated wood in hydraulic engineering is about 25 years (DBW/RIZA, pers. comm.). In practice, much of the wood will be disposed of as waste (dumping/incineration).

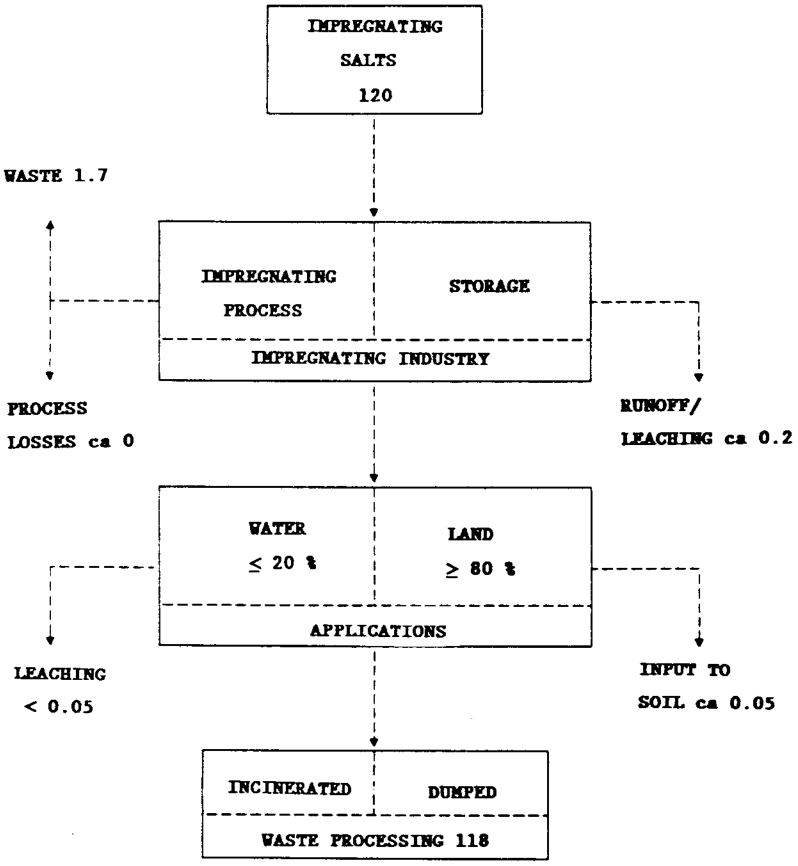


Figure 2.3. Mass balance for chromium (in tonnes) present in impregnating salts

- Cooling water

Corrosion inhibitors are frequently used in recirculating cooling-water systems. There has been a trend in the Netherlands for a considerable time to replace Cr(VI) for this application with other substances. At present, there are only a few companies allowed to use Cr(VI); these companies are currently switching to alternatives. The annual discharges were probably ≤ 0.5 tonne in 1986 (DBW/RIZA, communication).

- Others

The refractory industry in the Netherlands uses annually about 7 tonnes of Cr(III) (10 tonnes of Cr_2O_3). This is melted into the produced bricks to improve the refractoriness. Approximately 80% of the production is for the Dutch market. Of this, 80-90% is used in furnace parts of chemical-waste incinerators in particular. The aluminium industry uses about 10%. The useful life of the bricks in the waste incinerators is about 8 months. Thereafter, the bricks are generally stored aboveground on site (tel. business inf.). The refractory industry recycles all the waste generated in the production process, and chromium emissions into air and surface water are negligible (tel. business inf.).

The magnetic tape industry uses annually 325 tonnes of Cr(IV) (500 tonnes of CrO_2) in the production of magnetic tapes. The "rejects" contain about 30 tonnes of Cr(IV). This waste stream must be treated as chemical waste and is transported to a dump in East Germany (tel. business inf.). Used magnetic tapes probably end up eventually in urban waste.

The Dutch glass industry uses Cr(III) oxide green for colouring glass. A large percentage of this green-coloured glass is exported. Emissions of chromium into the atmosphere are negligible because of its high melting point. Chromium discharges into surface water have not been registered (VROM, 1988b; tel. business inf.). After use, part of the green-coloured glass ends up in urban waste and part is recycled (see further "Urban waste").

Chromium-based catalysts are used chiefly in naphta cracking plants. The amount involved is several tonnes per year at most. The chromium is not incorporated into the end-product and its emission into the environment is negligible. The catalysts are eventually reprocessed, or disposed of as chemical waste.

2.2.3. Primary raw materials

- Titanium dioxide ore-processing industry

The titanium dioxide ore-processing industry in the Netherlands manufactures titanium dioxide pigment (titanium white) on the basis of the so-called sulphate process with titanium dioxide ore as the starting material. In the sulphate process, the titanium-containing raw material, which in addition to titanium dioxide also contains a variety of by-products, is dissolved in concentrated sulphuric acid. A large volume of water is added to the resultant acid solution, so that titanium dioxide precipitates, while the other metals remain in solution. The precipitated titanium dioxide is separated from the acid solution by means of enormous filters. Pure titanium dioxide is obtained by washing the filter cake thoroughly. The resulting filtrate and washing water both contain the by-products from the titanium raw material, as well as all the sulphuric acid used. Together they make up the wastewater stream from the current sulphate process, which is directly discharged into surface water. About 60 tonnes of Cr(III) are annually discharged into the Nieuwe Waterweg in this way (tel. business inf.). There will be a changeover to another process as of 1-1-1990, which is expected to reduce emissions by 90%.

- Phosphate ore-processing industry

The phosphate ore-processing industry in the Netherlands consumed 2.03 Mtonnes of phosphate ore in 1986. Phosphate ore has a chromium content of 40-220 $\mu g.g^{-1}$ (Berenschot/Tebodin, 1987). Phosphoric acid is manufactured from phosphate ore by a wet process (dissolving in sulphuric acid and/or nitric acid) or by a thermal process. The chromium flows involved in the various operations are shown in figure 2.4.

In the wet process, emission of chromium into surface water occurs by discharging phosphoric acid gypsum, which results from the decomposition of the (calcium) phosphate ore. In this way, 6-26 tonnes of chromium were discharged into the Nieuwe Waterweg in 1986 (discharge licences; tel. business inf.).

The thermal processing of phosphate ore produces phosphorus slags and ferrophosphorus as by-products. Almost all the chromium introduced into the furnace via the phosphate ore is incorporated into the ferrophosphorus. This ferrophosphorus is utilized in principle in the Dutch base metal industry (tel. business (industry) inf.).

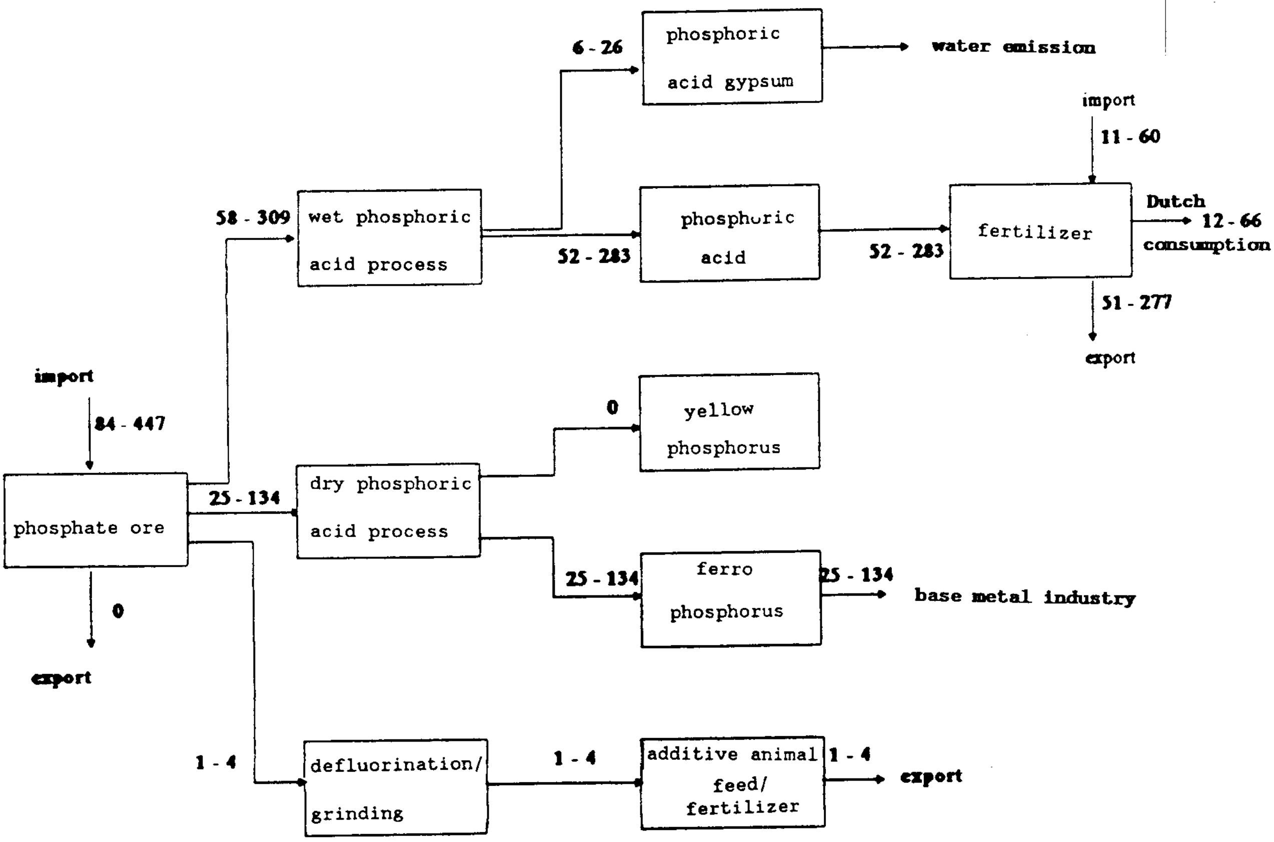


Figure 2.4. Chromium flow diagram for the phosphate ore-processing industry in 1986 (extrapolation from phosphorus balance sheet CBS, 1985; tel. business inf.): in tonnes of Cr per year

Part of the chromium present in the phosphate ore eventually ends up in commercial fertilizer. About 85% of this is exported. The remainder and the amount imported are used in agriculture, involving an (extrapolated) diffuse input to soil of about 12-66 tonnes of chromium per year.

- Power stations

The Dutch electricity generating stations burned 5300 ktonnes of pulverized coal in 1986. The chromium(III) emissions (KEMA, 1988) are given in table 2.5.

Table 2.5. *Emissions of chromium from power stations in the Netherlands (Cr(III), year 1986)*

Receiving material	*Amount (10^3 tonnes)*	*Concentration ($mg.kg^{-1}$)*	*Chromium load (tonnes)*	*Comment*
Fly ash	*532*	*75 -*	*85*	*94% reuse*
Bottom ash	*80*	*300*	*13*	
Stack ash (air)	*ca 1.3*	*av.160*	*0.2*	

The combustion of coal in power stations fitted with flue-gas desulphurization equipment also produces gypsum, sludge and waste water (KEMA, 1988). However, with regard to chromium, very small amounts are involved.

Pulverized-coal fly ash is reused, for example, as a filler, mixing element or fine aggregate in the asphalt, concrete or cement industry. The environmental aspects of the current (Dutch) applications of pulverized-coal fly ash have been extensively studied. Leaching of chromium from cement, concrete or asphalt is not to be expected, because the pulverized-coal fly ash is used in bound form on the one hand, and in strongly diluted form on the other (Bolt, 1983; Bolt, 1985; Bolt and Snel, 1985). The pulverized-coal fly ash not reused is stored, involving a (controlled) soil chromium load of about 5.2 tonnes a year. During the storage of fly ash, metals can leach out as a result of exposure to rain. It can be stated that the leaching of chromium from both acid and basic pulverized-coal fly ash is less than 1% except under specific conditions (Van der Sloot et al., 1982). Chromium leaches from the pulverized-coal fly ash as CrO_4^{2-} . At low pH values, a small amount of Cr^{3+} can also be expected (Van der Sloot et al., 1985). Figure 2.5. gives a chromium flow diagram for power stations in the Netherlands in 1986.

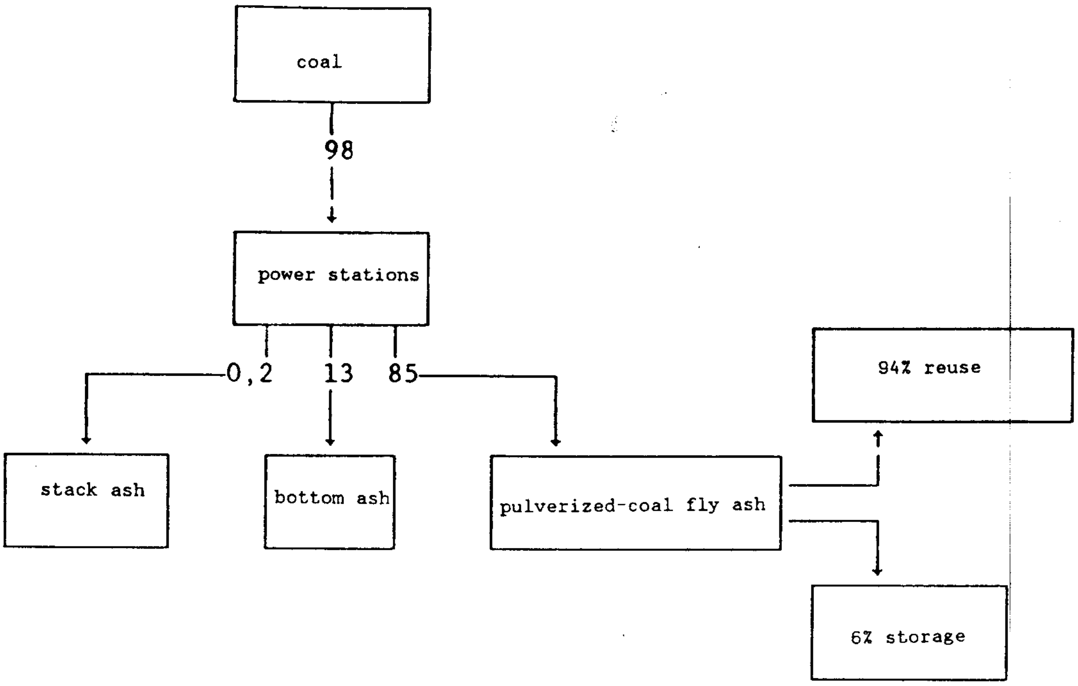


Figure 2.5. Chromium flow chart for power stations in the Netherlands in 1986, in tonnes of chromium per year (Vliegasunie, 1986; KEMA, 1988)

- Oil industry

The oil industry in the Netherlands refines annually about 50 million tonnes of crude oil (maximum capacity is 67 million tonnes). Crude oil contains 0.01-0.03 $mg.l^{-1}$ (0.005-0.73 $mg.l^{-1}$ according to Nriagu and Nieboer, 1988), involving a total chromium load of about 0.5-15 tonnes per year. In view of the distillation temperature during the refining process and the high melting point of chromium, chromium emissions into the air are probably very small. Most of the chromium is retained in the so-called residue. A small fraction of this residue, about 10%, is reprocessed in the cement industry. The rest is diluted with gas oil for fuel oil production. Almost all this fuel oil is exported because its sulphur content is too high.

Of the petroleum which is refined, 6% is used as fuel for the refining process (about 1/3 of this is residue). Assuming an emission of $\leq$ 1% into the air, this amounts to a maximum of 0.01 tonne of chromium per year.

2.2.4. Diffuse sources

- Agricultural industry

The agricultural sector in the Netherlands uses organic (animal manures and sewage sludge) and artificial fertilizers, which may all contain chromium. Information provided by a number of sources did not provide a clear insight into the Cr content of commercial fertilizer and animal manure (NMI, RIKILT, IVVO, IB, CVB, Consultancy for Soil, Water and Fertilization in the Livestock Industry).

The (extra) soil chromium burden from farm animals can be calculated on the basis of the animal feed imports. An estimated 99.9% of the chromium present in animal feed is eventually deposited on the soil (tel. business inf.). The chromium content of animal feed ranges from 0.2 to 0.7 $\mu g.g^{-1}$. Multiplied by the total amount of available concentrates (18,211 ktonnes in 1986, pers. comm. Commodity Board for Animal Feed), this amounts to a diffuse soil load of on average 8.2 tonnes per year.

The diffuse input to soil via chemical fertilizers is estimated at 12-66 tonnes of chromium per year (see 2.2.3. under "Phosphate ore-processing industry").

The contribution of organic fertilizers (private and public sewage sludge) to the diffuse soil chromium load is estimated at 11-12 tonnes per year (see 2.2.6. under "Sewage sludge").

Chromium incorporated in fertilizers will generally not leach into groundwater and/or surface water. However, emissions into surface water can be expected as a result of runoff. If it is assumed that 1% of the manure is washed away, this will result in an input to surface water of about 0.6 tonne of chromium a year (DBW/RIZA, 1986).

- Households and companies

The CBS (1988a) estimated the diffuse chromium discharges into waste water by households in 1986 to be 25 tonnes before treatment. According to DBW/RIZA (1986), households discharge only 3 tonnes a year, 2 tonnes of which go to sewage treatment plants. This report uses the CBS figures because, among other reasons, these figures are more consistent with the chromium load in the sewage sludge from public treatment plants.

On the basis of the assumption that all diffuse discharges are treated in a sewage treatment plant, the chromium present in the sludge after treatment is about 19 tonnes. The diffuse chromium discharges into waste water by factories in 1985 were calculated to be (with the same assumption) 15 tonnes per year before treatment and 4 tonnes a year after treatment.

- Traffic

The wearing of tyres is by far the most important emission source of chromium from traffic. The total emissions outside the built-up area into surface water is estimated, via extrapolation, at 0.1 and into soil at 0.6 tonne per year. Within the built-up area, the annual input to soil is estimated to be about 0.25 tonne and that into surface water about 0.05 tonne (from Feenstra and Van der Most [DWB/RIZA, 1986]).

- Other diffuse sources

Various chromium-containing waste products (phophorus slags, copper slags, lead slags and blast-furnace slags) are used as embankment-protection materials. Research by the RIZA (Dijkzeul, 1979) indicated that there is little, if any, leaching of chromium from the material. A study by DHV as part of the Rhine Action Plan (DHV, 1988) calculated that the total leaching of chromium from stony embankment-protection materials (slags) for the Dutch part of the Rhine basin is 0.001-1 kg per year. Because of the leaching of other heavy metals, a restrictive policy is currently being pursued for copper and lead slags (DBW/RIZA, pers. comm.). An emission source which is difficult to quantify is erosion. A study by Van Starkenburg and Van Luin (1985) among 41 companies in 25 industries revealed that elevated Cr concentrations in the waste water from breweries and waste incinerators are due to erosion of chromium-plated materials. At a rough estimate, about 0.01-1% of the chromium of Cr-containing materials used in the Netherlands diffusely enters the environment in one way or another via erosion. Chromium from coats of paint enters the environment diffusely through weathering, as does also a fraction that does not end up in the waste because of dispersion by wind et cetera during the sanding, burning off and scraping of paintwork. Chromium also enters the environment diffusely when metal objects are blasted with grit. In 1986, blasting operations produced about 100,000 tonnes of contaminated blasting grit, with a chromium content of ≤ 400 mg.kg^{-1}, equivalent to a load of ≤ 40 tonnes of chromium. Nowadays, grit is increasingly collected (there are regulations for entirely wrapping objects to be blasted so that the grit used can be collected); at present, about 60,000 tonnes per year is collectable and this amount will increase still further. Some 20,000 tonnes were processed in 1988, while the remainder was dumped or stored. It is expected that the chromium load in contaminated blasting grit will decrease (owing to the tendency to substitute alternatives for zinc (tetroxy)chromate) as will also the amount of grit which diffusely enters the environment. In 1987, the first WVO licences for these blasting activities were issued. Today, blasting is not carried out on or near open water.

The use of impregnated wood in hydraulic engineering is 7 to 20% of the total amount. This application releases annually 36 kg of chromium into surface water through leaching (DBW/RIZA, pers. comm.). Assuming that when impregnated wood is used on land the leaching of chromium is 1/10 that in water, this amounts to a diffuse input to soil of about 0.05 tonne per year. Diffuse atmospheric emissions as a result of incineration in the open air, multi-fuel stoves et cetera will be limited.

Feenstra and Van der Most (DBW/RIZA 1986) estimated the chromium input to surface water via overflow at 0.04 tonne per year. Chemical laboratory waste is increasingly collected and disposed of as small chemical waste (or together with other chemical waste). Dichromate is widely used for determining the chemical oxygen consumption of waste water. The waste products from this determination ("COD waste") are also disposed of as chemical waste. There is little insight into how much chromium from laboratories is lost via the waste water (DBW/RIZA, 1986). Households and companies account for the greater part of the discharges.

Approximately 0.6 tonne of Cr(III) is released annually from tobacco as a result of smoking. In view of its high melting point, chromium emissions into the air will be minimal. The chromium will end up in urban waste or diffusely enter waste water, surface water and soil by way of the ash.

2.2.5. Foreign sources

The West European chromium emissions into the atmosphere, as calculated by Jaarsveld et al. (1986) and Pacyna and Nriagu (1988), are given in table 2.6. A logical explanation for the discrepancy is that Pacyna and Nriagu (1988) used larger emission factors especially for the combustion of fossil fuels and metallurgical processes.

Table 2.6. Atmospheric chromium emissions in Western Europe, in tonnes of chromium per year

Country	Chromium (tonnes/yr) Jaarsveld et al. (1986)	Pacyna and Nriagu (1988)
Belgium	*79*	*550*
Denmark	*7*	*28*
France	*130*	*950*
Britain	*127*	*870*
Luxembourg	*24*	*195*
West Germany	*260*	*1860*
East Germany		*280*
Poland		*750*

The average annual chromium imports via the Rhine and Meuse Rivers are given in table 2.7. In view of the small amounts involved, importation of chromium via transboundary rivulets has been disregarded. Table 2.7. shows that the amount of chromium imported annually via the Rhine and the Meuse is falling.

Table 2.7. Average annual chromium imports via the Rhine and the Meuse in the Netherlands, in tonnes per year (Dept. of Public Works, 1980 to 1986 incl.)

	1980	1981	1982	1983	1984	1985	1986
Rhine	*1621*	*1490*	*934*	*926*	*700*	*389*	*600*
Meuse	*102*	*410*	*43*	*106*	*129*	*39*	*33*

2.2.6. Waste

- Sewage sludge

The total amount of chromium in sewage sludge from public and private treatment plants in 1985 was 33 tonnes and 1 tonne, respectively (CBS, 1988b; CBS, pers. comm.; RIVM/LAE, pers. comm.). Table 2.8. summarizes the destination of the sewage sludge. It can be deduced from this table that about 60% and 25% of the sludge from public and private sewage treatment plants, respectively, is diffusely applied to the soil.

Table 2.8. *Destination of sewage sludge (CBS, pers. comm.; RIVM/LAE, pers. comm; IMP Water 1980-1984; Martens, 1986; CBS, 1987)*

Public sewage treatment plants	Destination of dry matter (%)			
	1983	1984	1985	1986
Agriculture	36	32	32	35
Horticulture/parks	0	0	0	0
Conversion into compost/ organic soil	27	31	33	22
Dumping	30	33	32	39
Other sewage treatment plants	7	4	3	4
Other/not known	0	0	0	0
Chromium content ($mg.kg^{-1}$ d.w.)	132	142		68

Private sewage treatment plants	Destination of dry matter (%)			
	1982	1983	1984	1985
Agriculture	8.8	17.3	18.5	18.8
Sports fields/public gardens	0.0	0.0	0.0	0.0
Conversion into compost/ organic soil	15.6	17.5	5.9	5.8
Dumping	41.8	37.5	52.6	55.6
Incineration	0.2	0.2	2.3	1.6
Other	33.6	27.5	16.0	13.7
Chromium content ($mg.kg^{-1}$ d.w.)	147	193	64	43

- Urban waste

Urban waste consists of household refuse and waste from small firms and the services sector. Approximately 5.7 million tonnes of domestic waste are produced annually in the Netherlands. It is presented as bagged refuse (4.3 million tonnes), as glass deposited in bottle banks (0.2 million tonnes), as old paper collected by clubs and schools (0.5 million tonnes) and as bulky household waste (0.7 million tonnes). This waste is usually separately collected. In addition, municipalities and private collectors collect 1.8 million tonnes of waste from small enterprises (shops, offices, etc.) and the services sector (RIVM, 1987a).

The composition of the refuse-bag contents from five districts of different municipalities is determined in a representative way by the RIVM three times a year. On average, 1 tonne of wet refuse-bag contents contains 228 ± 14 $\mu g.g^{-1}$ chromium.

Approximately 65% of the urban waste was dumped in 1986. A small fraction of the waste is composted and marketed as compost (about 50,000 tonnes, from Slooff et al., 1987). About 35% (derived from 5.5 million inhabitants) is processed in one of the eleven waste incinerators in the Netherlands (RIVM, 1988). About 75% of the waste sent to these incinerators is household refuse, 20% is industrial waste which is collected together with the household refuse, and 5% is miscellaneous waste (e.g. litter from streets and markets, and flotsam from canals and harbours, about half of which is chemical waste and special waste) (RIVM, 1988).

Waste incinerators produce slags, fly ash and stack ash; the amounts produced are not the same for each installation but are, after extraction of the iron, approximately 0.07, 25 and 2.5 % by weight, respectively, of the original volume of waste materials (RIVM, 1988). It is estimated that about 30% of the chromium is recovered before incineration from the scrap, which makes up about 2.5% of the original volume of waste products (RIVM, 1987a). About 62% of the slags and 42% of the fly ash were reused, while about 3% of the slag was dumped abroad (RIVM, 1988).

A study by the RIVM (pers. comm.) measured that flue gases contain 0.05 $mg.Nm^{-3}$ (particle-bound) chromium. The incineration of 1 tonne of waste releases about 6,000 Nm^3 of flue gas. The total volume of waste incinerated is 2.6 Mtonnes per year, thus emitting annually 0.78 tonne of chromium into the atmosphere. The volume of waste dumped before or after incineration is probably not a large source of chromium to groundwater (leaching << 1%). One study (TAUW, 1984) found that the Cr levels in the percolate were very similar to those in rainwater, while another study conducted by the RIVM (Beker, 1988) did find raised concentrations. The average concentration in the drainage water from 13 Dutch waste dumps was 67 (range 0-1750) $\mu g.l^{-1}$ and in the groundwater at 10 Dutch dumping sites 7 (range 0-40) $\mu g.l^{-1}$.

The chromium flows associated with the processing of urban waste are shown in figure 2.6 and table 2.9.

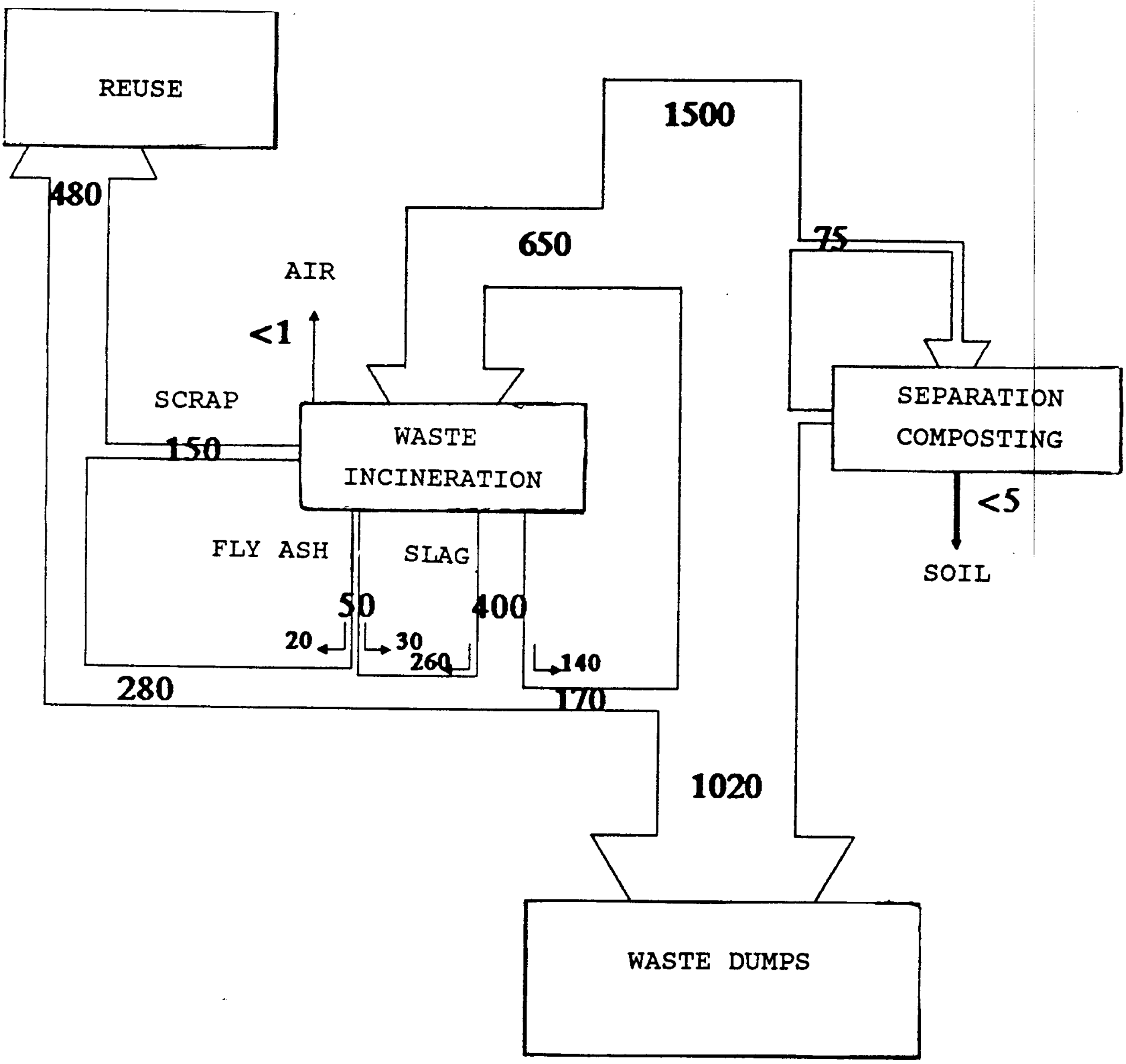


Figure 2.6. *Chromium flow diagram relating to the processing of urban waste in the Netherlands in 1986. The figures have been rounded off and are based on the quantities given in table 2.9.*

Table 2.9. Chromium flows in urban waste processing

Input *(RIVM, 1987a)*	*Total (Mtonnes/yr)*	*Cr (tonnes/yr)*
Urban waste	*7.5*	*1484*
of which household refuse	*5.7*	*1128*
of which bagged waste	*4.3*	*980*
bottle banks	*0.2*	*54*
old paper	*0.5*	*4*
bulky waste	*0.7*	*90*
Small commercial and industrial waste	*1.8*	*356* 1)

Processing *(RIVM, 1988)*	*Total (Mtonnes/yr)*	*Cr (tonnes/yr) (from input)*2)	*Cr (tonnes/yr) (from output)*3)
Incineration	*2.6*	*515*	*653*
of which household refuse	*2.0*	*396*	*502*
small commercial and industrial waste	*0.5*	*99*	*126*
other waste	*0.1*	*20*	*25*
Dumping + composting/ separation	*4.9*	*970*	*831*

Output *(residues) (RIVM, 1987a; 1988)*

	Total (Mtonnes/ yr)	*Cr (tonnes/ yr)*	*Total (Mtonnes/ yr)*	*Cr (tonnes/ yr)*	*Total (Mtonnes/ yr)*	*Cr (tonnes/ yr)*
	Total		*of which reused*		*of which dumped at home*	
Fly ash	*0.065*	*44*	*0.027*	*18*	*0.038*	*26*
Stack ash	*0.002*	*0.78*	-	-	-	-
Slags	*0.650*	*413*	*0.422*	*268*	*0.208*	*145*
Scrap	*0.065*	*195*	*0.065*	*195*	*0*	*0*
Dumped+ composted	*4.9*	*831*	-	*3*	*4.9*	*828*
Total		*1484*		*484*		*987*

1) *extrapolation from urban waste*
2) *extrapolation from input*
3) *extrapolation from output*

- Dredged spoil

Of the total amount of chromium imported via the large rivers, 35% is retained in dredged materials (IMP Water 1985-1989). About 40% of the dredged spoil is directly dumped into the North Sea and about 60% is stored in spoil repositories. According to the RIVM, 580 ktonnes of class IV spoil are dredged annually, with an average Cr content of 100 $mg.kg^{-1}$.

- Chemical waste

Relevant waste streams have already been discussed in the section on industrial sectors. It concerns waste streams which (if necessary, after treatment) are (currently still) sent to foreign dumps. The incineration of chemical waste in the Netherlands produces annually some 13,000 tonnes of slag and 1,000 tonnes of fly ash, both having a Cr content of 900 $mg.kg^{-1}$ (RIVM/LAE, 1988; tel. business inf.). This amounts to a total of 12.6 tonnes of chromium per year. The amount of chromium emitted into the air during the incineration of chemical waste is probably less than 0.1 tonne per year (extrapolation from VROM, 1988b and tel. business inf.).
In addition, 120,000 tonnes of jarosite are produced in primary zinc production, with a chromium load of 36 tonnes. The jarosite is dumped on the factory site. A preliminary investigation is currently being conducted to determine the extent, starting-points and preconditions for a process-technical and commercial feasibility study on the reprocessing of iron-containing waste products in the Netherlands. The results of this study will have to show whether jarosite is suitable for the manufacture of steel after thermal treatment (removal of volatile metals).

2.2.7. Natural sources

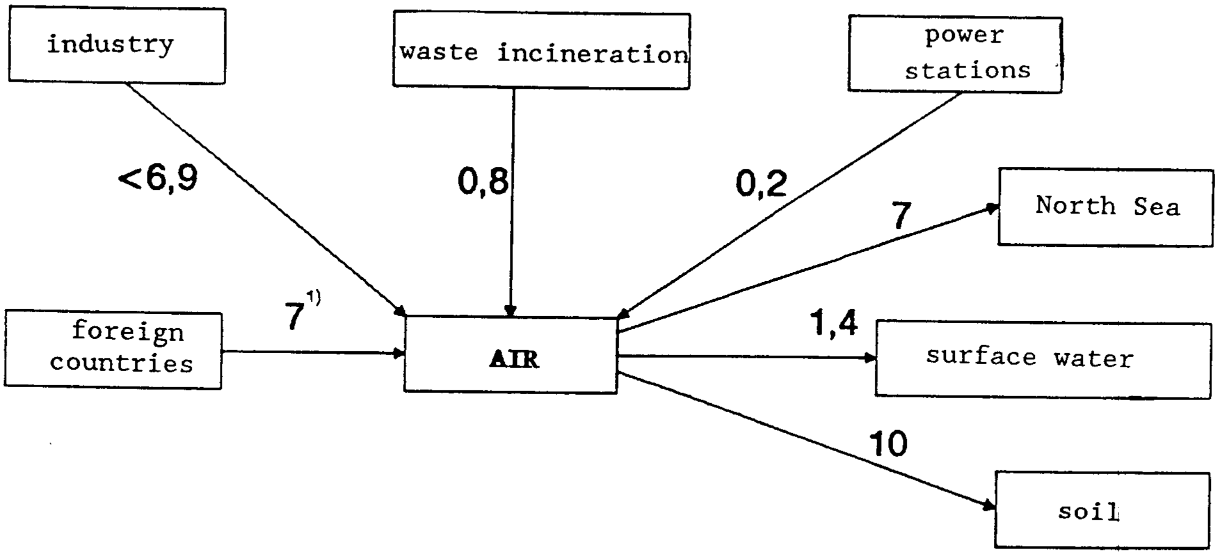
Windblown dust and volcanism have been mentioned as the principal natural sources of atmospheric chromium. Other relatively minor natural sources are seasalt sprays and smoke from forest fires (Pacyna and Nriagu, 1988). In the Netherlands, these contributions are negligible compared with the anthropogenic input.
Of the approximately 600 tonnes of chromium imported via the Rhine River in 1986, an estimated 60-135 tonnes (10-22.5%) is of natural origin. It can be estimated by extrapolation that the natural chromium imports via the Meuse River ranged from 3 to 7 tonnes in 1986 (Vellinga et al., 1988).

2.3. SUMMARY AND CONCLUSIONS

A summary of the chromium emissions into, and chromium flows in, the environmental compartments air, water and soil is given in the figures 2.7, 2.8. and 2.9., respectively. Table 2.10. lists the chromium emissions from the various industrial sectors into the environmental compartments soil, air and water in the Netherlands in 1986. The reader is referred to the background report by Haskoning (1988) for the sources from which the data are derived, and detailed calculations.

Finally, table 2.11. summarizes the principal quantities of chromium disposed of in 1986 with waste (urban and chemical waste). With the observed current trends, more chromium will be incorporated in the waste streams (mainly chemical waste) in the case of end-of-pipe measures. The introduction of process-integrated measures in the use of chromium chemicals will lead to less waste. Efforts aimed at reuse, for example of fly ash from power stations and waste incinerators, will cause competition between waste streams (limited number of applications and limited capacity per application).

The trend towards more incineration of waste does not essentially lead to another form of soil loading (dumping of waste or of ash).



[1]) This is the fraction remaining in the Netherlands via deposition (PEO, 1986)

Figure 2.7. *Schematic representation of the chromium input to the Dutch atmosphere in 1986, in tonnes of chromium*

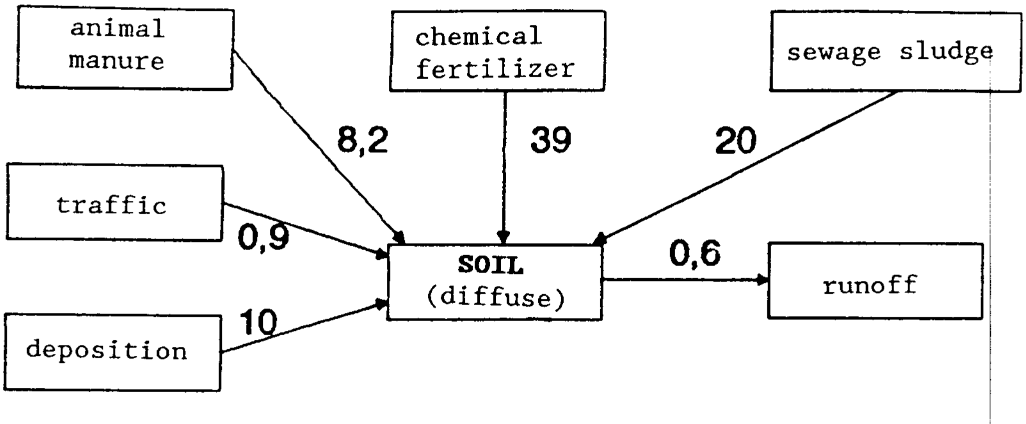


Figure 2.8. *Schematic representation of the chromium input to Dutch soil in 1986, in tonnes of chromium*

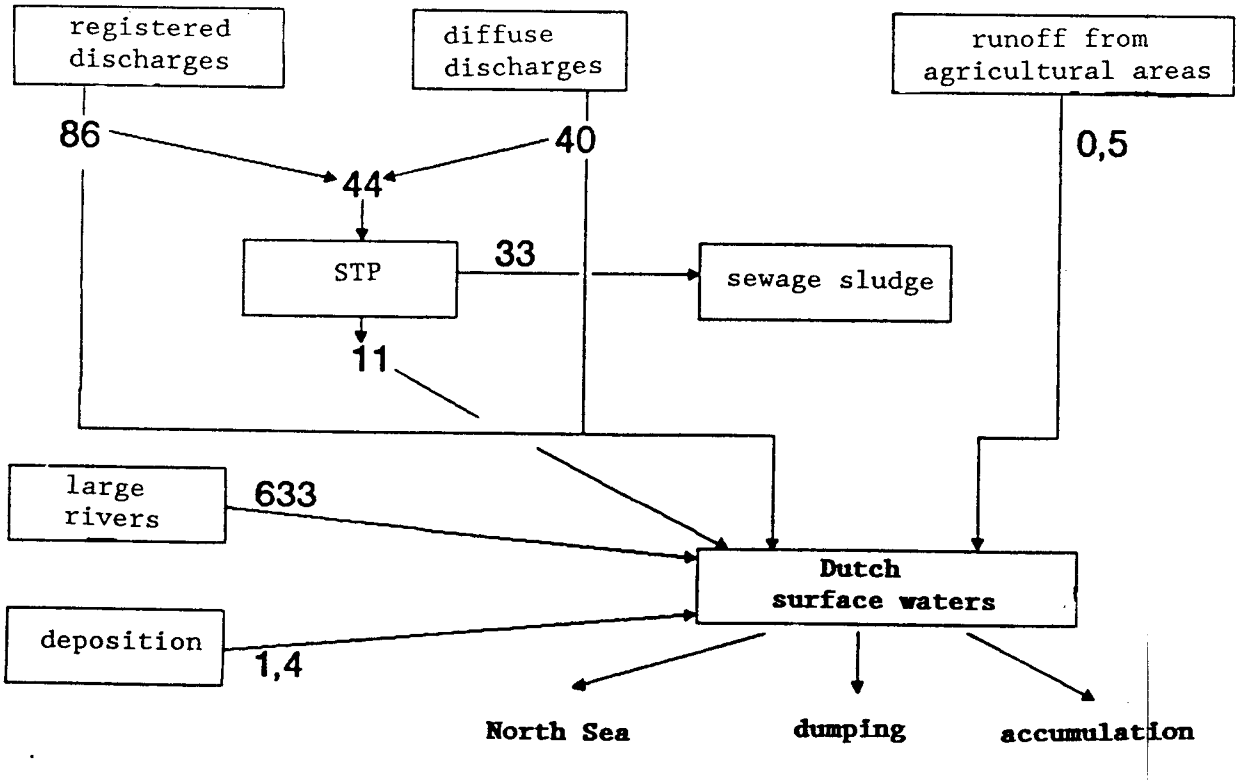


Figure 2.9. *Schematic representation of the chromium input to the Dutch surface water in 1986, in tonnes of chromium*

Table 2.10. Cr emission (in tonnes per year) in the Netherlands, per source (1986)

Use	*Soil (diffuse)*		*Air*		*Water (surface)*		*Number of sources*
	total	*Cr(VI)*	*total*	*Cr(VI)*	*total*	*Cr(VI)*	
Production of Cr comp.							
Pigment industry			*0.1*	*0.1*	*0.3*	*0.3*	*2*
Use of chromium comp.							
Metal products industry			*<<3*	*0.3*	*9.9*		*ca 350*
Paint application	*8.9*	*8.5*	*0.5*	*0.5*	*0.2*	*0.2*	*>1000*
Base metal industry			*<1*		*1.4*		*2*
Tanneries					*2.5*		*45*
Printing industry					*1.1*	*0.6*	*ca 10*[1]
Textile industry					*1.1*		*>100*
Wood-impregnating ind.	*±0.2*	*?*			*<0.1*		*33*
Cooling water					*≤0.5*	*≤0.5*	*ca 2*
Primary raw materials							
Titanium dioxide ore-processing industry					*60*		*1*
Phosphate ore-processing industry					*16*		*3*
Power stations			*0.2*				*5*
Oil industry			*<0.01*				*3*
Diffuse sources							
Agricultural industry (animal + chemical fertilizer)	*47*				*0.5*[3]		*>1000*
Households					*6*		*>1000*
Companies					*4*		*>100*
Traffic	*1*				*0.1*		*>1000*
Wastes							
Sewage sludge	*20*				*0.2*		*>500*
Urban waste			*0.8*		*<0.01*		*ca 260*
Others			*<2*[4]		*1.8*[5]		
Total	*77*	*8.5*	*±5*	*0.9*	*105*	*1*	

[1] *particularly intaglio establishments*

[2] *via cooling water*

[3] *via runoff*

[4] *residual item (VROM, 1988b)*

[5] *residual item (IMP Water 1985-1989)*

Table 2.11. Chromium-relevant waste streams in the Netherlands in 1986

Category	Waste stream	Amount	Comment	Chromium (tonnes)
Production of chromium compounds				
Pigment industry	- wastewater sludge	100 t	d.w., 7% Cr	7
	- pressed cake & powder	50 t	d.w., 10% Cr	5
Use of chromium chemicals				
Paint application	- spraying waste	ca 9,000 t		4
	- painting waste	ca 170 t		0.1
	- de-varnishing waste	ca 410 t		0.1
	- paint slurry	ca 410 t		0.1
	- hot alkali paint-stripping waste	ca 410 t		0.1
	- empty cans	ca 1,180 t		0.9
	- miscellaneous	ca 240 t		0.2
	- building waste	ca 2,240 t		1.9
Wood-impregnating industry	- impregnating process			1.7
Refractory ind.	- bricks			± 5
Magnetic tape ind.	- rejected tape			± 30
Leather industry	- chromium sludge	3,258 t	60% water	25
	- shavings, clippings and remnants	7,500 t	60% water (69 t exported)	71
Metal products industry	- metal hydroxide sludge	1,500 t	d.w.	30
Paper industry	- de-inking sludge	55 t		1
Processing of Cr-containing primary raw materials				
Zinc ore industry	- jarosite	120,000 t		36
Power stations	- pulverized-coal fly ash	532 kt	±94% reuse	5
Waste				
Urban waste	- fly ash	65 kt	(dumped at home):	26
	- slags	650 kt		145
	- scrap	65 kt		0
	- dumped	4,900 kt		828
Sewage treatment plants	- sewage sludge	6 Mt	(ca 60% diffuse)	14
Dredged spoil	- class IV	580 kt	dumped into North Sea	23
			Spoil repositories	35
Incineration of chemical waste	- slag	13 kt		12
	- fly ash	1 kt		1
Blasting grit		100 kt		≤40
Contaminated soil		200 kt		3
Drinking-water sludge		30 kt		7

3. FORMS OF OCCURRENCE AND DISTRIBUTION

3.1. FORMS OF OCCURRENCE

Chromium occurs in several oxidation states, two of which can be stable in the environment: Cr(VI) and Cr(III). Cr(VI) is more toxic than Cr(III) to most organisms in the environment (Nriagu and Nieboer, 1988), Cr(III) even being an essential trace element for mammals (see chapter 5). The lifetime of the less stable Cr(IV) is very short (Nieboer and Jusys, 1988), whereas that of Cr(VI) is of the order of minutes to a few days (Boyko and Goodgame, 1986).

The distribution between Cr(VI)- and Cr(III)-containing species is relevant to the speciation of chromium in the environment. The occurrence of a particular distribution depends mainly (Schmidt, 1984; Stern, 1982) on:

- existing redox potential, E_h;
- existing pH;
- presence of certain oxidizing/reducing substances;
- kinetics of the redox reactions of chromium compounds;
- formation of Cr(III) complexes and insoluble Cr(III) salts;
- total chromium concentration.

Cr(VI) and Cr(III) can be interconverted depending on the conditions, in which Cr(IV) and Cr(V) can act as intermediates.

Cr(VI) always occurs as a negatively charged hydrated oxo compound, and does not usually form complexes with anorganic or organic ligands (Nieboer and Jusys, 1988; Stern, 1982). In contrast, the Cr(VI)-containing chromate anions themselves behave as ligands, and can react with metal ions. Of the Cr(VI) species, the dichromate ion $Cr_2O_7^{2-}$ does not occur in the environment at total chromium concentrations below 500 $mg.l^{-1}$ (ca 0.01 M). Zinc and lead chromate are sparingly soluble in water, but potassium and sodium chromate as well as many other chromates are readily so.

In an aqueous environment Cr(III) is present as the positive ion which, depending on the pH, forms hydroxides and can form complexes with ligands such as carboxylic acid, phenols, phosphates, ammonia, amides, fluoride, cyanide, thiocyanate, oxalate, sulphate, etc. (Baes and Mesmer, 1977). Many Cr(III) complexes are kinetically stable ("inert"). Many Cr(III) compounds, such as chromic(III) oxide and chromic(III) phosphate, are virtually insoluble in water. However, the hydrated Cr(III) sulphates, chlorides and nitrates are soluble in water.

The E_h-pH equilibrium diagram for 10^{-6} M Cr in water (Huffman, 1973) is given in figure 3.1. This picture is almost identical for 10^{-8} M Cr (corresponding to the current concentrations) (Schmidt, 1984). Also the presence of Cl^- does not alter the picture shown (Angus et al., 1987).

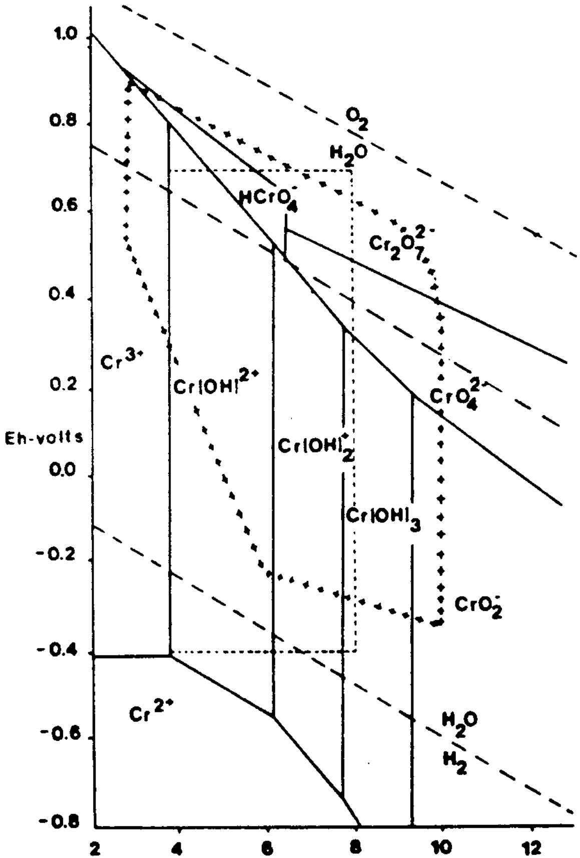


Figure 3.1. E_h-pH equilibrium diagram for 10^{-6} M chromium in water, in which the environment-relevant relationships are indicated (Huffman, 1973; Cary, 1982; Garrels and Christ, 1965; Hem, 1977; Robertson, 1975)

_____ *between 2 species means equal concentrations of each species;*

\- - - *bounds the thermodynamic stability of water;*

-.-.- *represents the relationship for water in contact with the atmosphere;*

_____ *encloses the area in which most soil E_h-pH measurements lie;*

++++ *encloses the area in which most E_h-pH measurements for surface water are located.*

Figure 3.1. describes thermodynamic equilibrium states for the Cr-O-H system, but does not provide information about reaction rates or influences of other ligands. Since Cr(III) compounds are generally kinetically inert, once Cr(III) is formed by reduction of Cr(VI), a possible re-oxidation of Cr(VI) will take place very slowly or only under relatively extreme conditions.

In the environment the chromium concentrations are usually low, the Cr(III)/Cr(VI) concentration ratio is high and the redox behaviour of the Cr species complex, so that the analysis of Cr(VI) presents problems for all compartments (Langärd, 1982).

A few of the processes which determine the behaviour of Cr(III) and Cr(VI) in the water/soil environment are shown in figure 3.2.

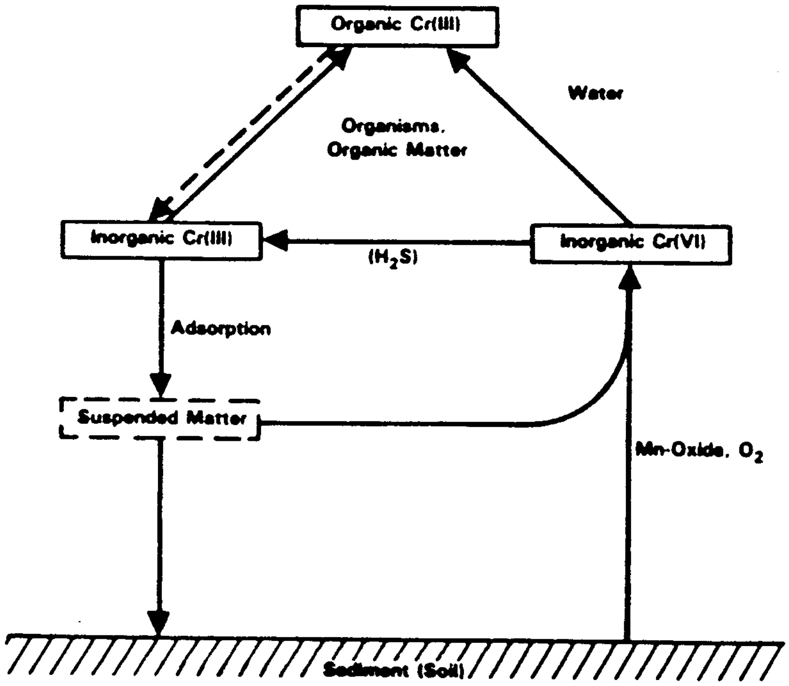


Figure 3.2. *Schematic representation of processes which help determine the speciation of Cr(III)/Cr(VI) in the environment (Schmidt, 1984)*

Soil

In the soil chromium may be present both as Cr(III) and as Cr(VI). The percentage of Cr in each of these forms depends on the local pH and E_h conditions (see figure 3.1.), and the presence of certain reducing or oxidizing substances. Cr(VI) is known to be reduced by organic matter (Bartlett and Kimble, 1976). Hexavalent chromium can be stable in sandy soils and soils low in organic matter (Frissel et al., 1975). The presence of manganese dioxide can cause oxidation of Cr(III) to Cr(VI) (Bartlett and James, 1979). Cr(VI) compounds are more mobile than Cr(III) species. It is assumed that if Cr(VI) is formed in the soil, it is partly adsorbed as such, partly reduced again to Cr(III) elsewhere, and can partly reach the groundwater as Cr(VI) (Cary, 1982). Cr(III) is the dominant species under Dutch environmental conditions.

Surface water

Conditions also exist in surface water, especially sea water, under which either Cr(III) or Cr(VI) can be thermodynamically stable. With regard to Cr(VI), at pH < 6 the weakly acid $HCrO_4^-$ is the main species, whereas at pH > 6 the CrO_4^{2-} dominates. For Cr(III), the hydrated hydroxides $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_3$ are the dominant species at pH ca 4, 6 and 8, respectively (Stern, 1982). Oxidation of Cr(III) to Cr(VI) by atmospheric oxygen is only possible at pH > 12, and consequently will not occur in the environment (Thomson and Stern, 1979). However, manganese dioxide can bring about this oxidation.

Air

The existence of gaseous Cr species has never been demonstrated: atmospheric chromium is always associated with particulates. It is assumed that metallic chromium and Cr(III) are stable in the atmosphere in view of their low reactivity, and that Cr(VI) is for the most part reduced to Cr(III) (Rühling et al., 1987). There are indications that the Cr(VI) fraction can be stable depending on the meteorological conditions (De Boer, 1989). Measurements of the speciation of the possible small Cr(VI) fraction are laborious and scarce. The atmosphere in California was found to contain 3 to 8% Cr(VI), but this observation is not known to have been reported for other locations (Goh et al., 1986; Air Resources Board, 1986). The research group concerned estimated the range to be wider in view of the uncertainties in the measurement technique used, namely, from 0.01 to 30% atmospheric Cr(VI).

3.2. BEHAVIOUR IN THE SOIL

General

In the soil environment Cr(III) is the most common stable form. The Cr(VI) present is for the most part directly reduced to Cr(III). Only in oxygen-rich soils containing no organic matter and in which manganese oxide is present as an oxidant is Cr(III) oxidized to Cr(VI) (Bartlett and James, 1979). The presence of Cr(VI) in soil can nearly always be ascribed to human activities, although Robertson (1975) demonstrated that Cr(VI) can also occur naturally.

Cr(III) can be adsorbed onto clay minerals, organic soil matter and metal hydroxides, form complexes with numerous ligands (see 3.1.), and replace Al(III) cations in the lattice of aluminium silicates. Many Cr(III) compounds are sparingly soluble in water (see table 1.1.). Cr(VI) compounds can be adsorbed onto positively charged surfaces, such as oxides and hydroxides of iron, manganese and aluminium, depending on the pH. Chromates are usually readily soluble (see table 1.1.).

Mobility

The mobility of chromium in soils is dependent upon the degree of adsorption and of the solubility of the species. These factors in turn depend on the composition of the groundwater and on the properties of the soil material.

The adsorption process is determined especially by the charge of the soil material, and is controlled by the pH and the CEC (Cation Exchange Capacity) of the soil. Specific adsorption is of secondary importance.

When the pH > PZC (Point of Zero Charge) of the soil material, Cr(III) is the main species being adsorbed. When the pH < PZC, chromates are adsorbed, especially onto iron and aluminium oxides and hydroxides because of their high PZC values (6.7-8.5). These (hydr) oxides are often present in the soil as thin coatings, precipitated onto other soil material (Stumm and Morgan, 1981). At high pH of the groundwater (> 8.5) adsorption of Cr(VI) is insignificant. This pH area is not applicable for the Netherlands. Other factors which determine the adsorption of chromate are the presence of phosphate, sulphate, selenite, selenate, molybdenum, silicate and arsenate in the groundwater, because these anions and chromate anions compete for the same adsorption sites (Music et al., 1986; Sengupta and Clifford, 1986).

Adsorption of Cr(III) increases with increasing CEC. The CEC of a few materials is given in table 3.1.

Table 3.1. Cation exchange capacities (CEC) of a few Dutch soils (meq per 100 g) (Bolt and Bruggenwert, 1976)

Dutch soils	*CEC (meq per 100 g)*
- Recent marine clay	*60.7*
- Young sea clay	*18.5*
- Young lake deposit (Lake IJssel)	*36.5*
- River basin soil	*78.1*
- Humic podzol	*8.8*
- Organic soil matter	*150 - 500 (Grim, 1986)*

Chromium bound to organic soil matter represents only a small fraction of all the bound chromium (Grove and Ellis, 1980). Only a very small percentage of the chromium from fertilizers will leach into groundwater owing to its distribution between the solid and liquid phases.

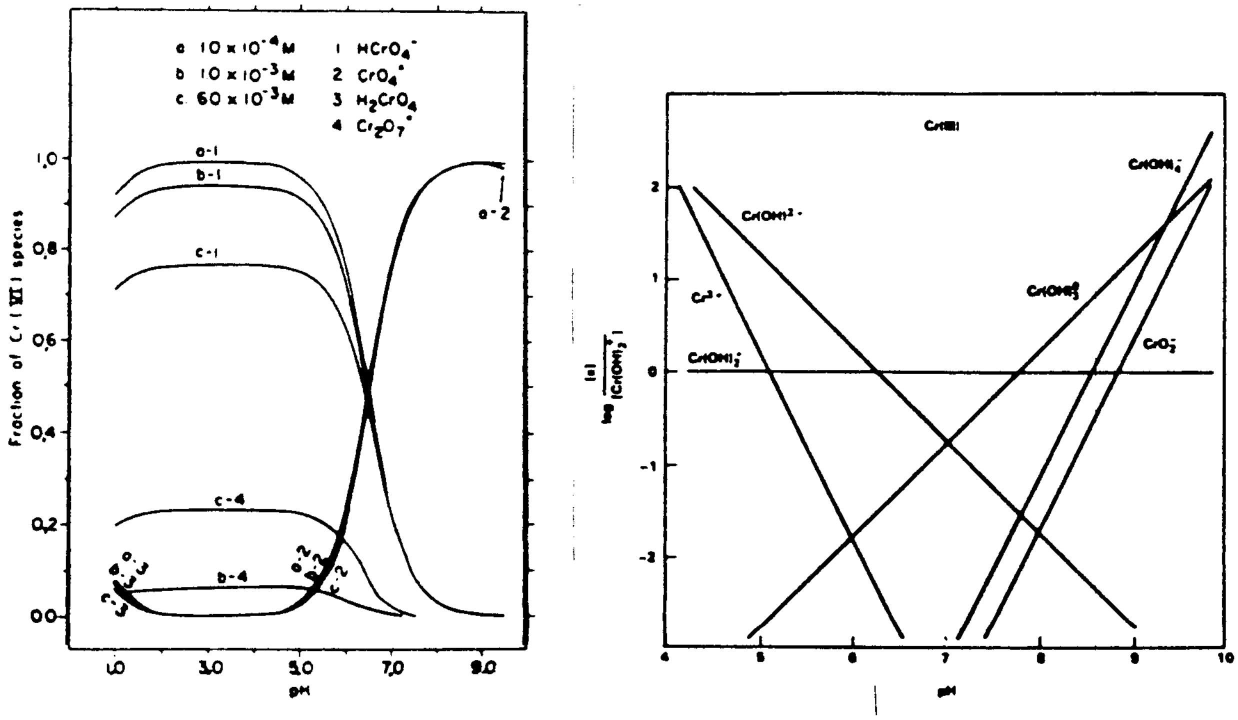
All Cr(III) complexes formed under acid conditions are readily soluble (James and Bartlett, 1983a, 1983b, 1983c). Thus at low pH, at which the degree of adsorption is low, the Cr(III) fraction dissolved in groundwater can be relatively high.

The adsorption of both Cr(III) and Cr(VI) is a non-linear process (Griffin et al., 1977; Stollenwerk and Grove, 1985a, 1985b). Distribution coefficients K_d (defined as the ratio between the concentration in the solid material and the concentration in the water phase) then have a very limited significance, namely, for a small concentration range. The K_d values were found to be dependent on the pH, moisture content and the (initial) concentrations of chromium compounds in the system (Bartlett and Kimble, 1976; Griffin et al., 1977; James and Bartlett, 1983b). On the basis of measured chromium levels in various soils and groundwater samples, the K_d values for Dutch soil systems will range from 30.10^3 to 300.10^3 $l.kg^{-1}$.

3.3. BEHAVIOUR IN SURFACE WATER

Distributions of chromium over the different Cr(VI) and Cr(III) species in water as a function of pH are given in figure 3.3. Chromium(VI) compounds are generally more soluble in water than Cr(III) compounds, so that Cr(VI) is relatively mobile.

Cr(III) forms, as do Fe(III) and Al, various hydroxides by hydration and hydrolysis, of which $Cr(OH)_3$ will precipitate in neutral and alkaline environments (Grove and Ellis, 1980; Murrman and Koutz, 1972). Although Cr(III) is sparingly soluble in principle, it can nevertheless form readily soluble complexes, which remain stable over a broad pH range (Bartlett and Kimble, 1976; James and Bartlett, 1983a). As a result of complexation of Cr(III) by, for example, humic and fulvic acids, its mobility can increase, and possible oxidation reactions are greatly retarded (Cotton and Wilkinson, 1980). Since Cr(III) complexes are relatively inert, the thermodynamically stable Cr(VI) species is usually not formed, even in an oxygen-rich aqueous environment.



<u>Figure 3.3.</u> Distribution of anorganic Cr(VI) and Cr(III) species in water as a function of pH (Griffin et al., 1977; Schmidt, 1984). The relative distribution of Cr(VI) over 4 species is shown in the left figure, and that of Cr(III) over 5 species in the right figure

Cr(VI) always occurs as part of a negative ion. It does not bind to clay minerals or organic soil matter, but may be adsorbed onto positively charged surfaces. Chromate ions can form sparingly soluble salts with some cations (such as Pb^{2+} and Zn^{2+}). When Cr(VI) is not adsorbed or does not precipitate, it remains present as free chromate ion (NRCC, 1985).

As has been mentioned for the behaviour in soil, the reduction of Cr(VI) is promoted by the presence of organic matter, with the formation of organically bound Cr(III), and by a low pH (Nriagu and Nieboer, 1988). A possible oxidation of Cr(III) is promoted by interaction of Cr(III) with manganese oxides (Bartlett and James, 1979). Fe(II) compounds and dissolved sulphide can also reduce Cr(VI).

Insight into the occurrence of Cr(III) and Cr(VI) species is in fact limited. In a study aimed at developing analytical methods for determining Cr(VI) species, the proportions of Cr(III) and Cr(VI) were determined in a limited number of cases; see table 3.2. (Vos, 1985).

Table 3.2. Proportions of Cr(III) and Cr(VI) species (Vos, 1985)

	% Cr(VI)	*% Cr(III)*
Effluent from sewage works	*20 - 30*	*70 - 80*
River water	*40 - 80*	*20 - 60*
Sea water	*25 - 40*	*60 - 75*

Adsorption and distribution coefficients

Cr(III) cations are adsorbed onto the negatively charged surfaces of clay minerals. The degree of adsorption is dependent upon the concentration and the charge of the other cations in the system. At pH > 4, Cr^{3+} is strongly adsorbed (Griffin et al., 1977). At high pH values $Cr(OH)_3$ too will precipitate, which further reduces the mobility of Cr(III).

Cr(VI) anions are adsorbed onto positively charged surfaces, such as those of the oxides and hydroxides of Fe, Mn and Al. Adsorption of Cr(VI) is usually limited, and decreases with increasing pH.

The experimentally determined distribution coefficients of Cr(III) vary widely, from 25.10^3 to 800.10(3) $l.kg^{-1}$. For Cr(VI) the range lies at lower values, from $250\text{-}50.10^3$ $l.kg^{-1}$. Important factors here are the pH, nature and concentration of the adsorbent, and the concentration of chromium species. Distribution coefficients for various Dutch waters, calculated from measurement data, range between 200.10^3 and 800.10^3 $l.kg^{-1}$ with an average of 296.10^3 $l.kg^{-1}$ (DBW/RIZA, 1982).

In addition to adsorption of Cr(III) on mineral soil components, its binding to organic matter is also important. The degree of binding depends on the number of dissociated functional groups, mostly carboxyl and

phenolic OH groups (Schnitzer, 1978). This number is pH dependent. The number of dissociated functional groups increases with increasing pH, so that the number of adsorption sites for positively charged ions increases. This is, of course, also true for adsorption onto suspended material: an increase in pH results in a decrease in concentration in the water (Salomons, 1983).
Adsorption and complexation contribute greatly to the transport of chromium in surface water, because a large proportion, usually over 50%, of the chromium is involved.

The foregoing paragraphs show that the redox potential and the pH are the principal controlling parameters for the behaviour of chromium species in aqueous environments. The pH affects the course of oxidation and reduction processes especially through its influence on the adsorption behaviour. In addition, salinity plays a role particularly in the transition zone between fresh and salt water.

Transition from river to sedimentation basin

The transport of chromium in the aquatic environment is closely related to that of suspended particulate matter. Some 75-80% of the load in the large rivers is bound to suspended material. Part of this material, with the metals bound to it, sediments in the Dutch surface water system.
Of the Rhine and Meuse water entering the Netherlands, the main input to the Dutch surface water system, 60 to 65% on average discharges into the sea via the Nieuwe Waterweg. The remainder passes the large freshwater basins, i.e. 10-15% Lake Ketel/Lake IJssel, and 25-30% Hollandsch Diep/Haringvliet. A substantial proportion of the load of suspended matter sediments in these basins, as well as in the Tidal river area (Rotterdam/Nieuwe Waterweg): in Lake Ketel about 50%, in Hollandsch Diep/Haringvliet about 70%, and in the Tidal river area about 20% (excluding marine sediments). Lake IJssel functions as a source of suspended material owing to the formation of calcium carbonate and the production of organic matter (algae/detritus). Sedimentation also occurs along the courses of the rivers (water meadows, dead corners, and certain reaches in the Meuse). This amount is small compared with the sedimentation in the above-mentioned parts of the surface water system.

With the deposition of suspended matter, a substantial proportion of the chromium input is also deposited. In 1980, for example, 70% of the chromium load was retained in Lake Ketel/Lake IJssel, and 65% in Hollandsch Diep/Haringvliet (DBW/RIZA, 1982).
If sedimentation were the only mechanism for the retention of chromium, the levels of dissolved chromium would remain more or less the same during passage of the basins, but this is not the case. The concentration of dissolved chromium falls, particularly in Lake IJssel. This is due to the production of "clean" suspended matter (calcium carbonate, detritus), and the increase in pH as a result of algal growth and adjustment of the carbon dioxide equilibrium between water and atmosphere. The complex of factors is reflected in the K_d values, derived from measurements. In comparison with the value at Kampen, the distribution coefficient on the River IJssel-Lake Ketel-Lake IJssel course increases during passage of Lake Ketel (decrease in suspended matter content), to decrease sharply thereafter during passage of Lake IJssel (increase in suspended matter content, increase in pH). A similar development, but less pronounced, occurs on the course Vuren (Rhine) and Keizersveer (Meuse)-Hollandsch Diep-Haringvliet. It can be deduced from the increase in the K_d in Lake IJssel with increasing pH that Cr(VI) is here the dominant species, for if Cr(III) were the main species, the reverse picture would be observed. It should be remarked here that several observations (in different years and locations, and using different procedures) sometimes give rise to conflicting findings. For instance, the example given here is based on measurement data from DBW/RIZA (period 1974-1986) in Wakwal reports. The findings of the ZMAS study (1977/1978) point to an increase in the distribution coefficient for Lake IJssel in particular (ZMAS, 1984).
The sediment is anaerobic from a few millimetres to several centimetres below the water-sediment interface. The thickness of the layer depends on the supply and consumption of oxygen (usually limited supply, high consumption), and the degree of mixing (relatively large in large expanses of shallow water such as Lake IJssel, and relatively small in deep water such as the Haringvliet). In this reducing environment a steady conversion of Cr(VI) to Cr(III) takes place, aided by the presence of Fe(II), organic matter and sulphides. Cr(VI) can be stable in the presence of manganese oxide. In practice, the distribution coefficient for the sediment-pore water system in the basins is small compared with that for the water-suspended matter system (ZMAS, 1984). This suggests that Cr(VI) is also the

dominant species in sediment-pore water systems (increasing concentrations of dissolved chromium in the pore water). A clear picture of factors, causes and effects cannot as yet be given.
In a system with a constant chromium input, release of chromium from the sediment to the surface water can take place as a result of exchange through resuspension and diffusion of chromium-rich pore water. However, the same processes which cause deposition of chromium also hold for the chromium released: there is a cycle in the system without this being accompanied by a net release. This occurs especially in Lake IJssel (intensive mixing of the upper sediment layer, high degree of resuspension). Release takes place as long as a new "equilibrium state" has not yet been attained. Adjustment is relatively rapid in Lake IJssel because of the large degree of resuspension in this lake. Exchange between sediment and surface water in Hollandsch Diep/Haringvliet is much less intense. Here, it will involve the burial of old sediment by new (less contaminated) sediment rather than the mixing of old and new sediment in a layer of substantial thickness.

Transition from fresh to salt water

The transition from fresh to salt water is accompanied by a number of changes in the chemical conditions which affect the behaviour and transport of chromium. A few important changes are:

- Because of the hydrological conditions in the mixing zone between fresh and salt water, a zone with elevated levels of suspended material results (turbidity maximum). When the total chromium concentrations remain constant, this causes an increase in the percentage of adsorbed chromium. After the water has flowed through this zone the reverse process occurs.
- Flocculation of iron and manganese (hydr) oxides produces "fresh" adsorbent, so that the percentage of adsorbed chromium increases.
- The increase in salinity affects the distribution of chromium. Adsorbed Cr(III) is displaced by positive ions, and Cr(III) forms a complex with chloride. The K_d value is reduced by both processes.
- The effect of the increase in pH is the reverse of that of the increase in salinity: the adsorption of Cr(III) decreases.
- In a seaward direction, there is ever-increasing mixing of relatively clean sea water, and marine suspended matter and sediment, with the

relatively contaminated river water and riverine suspended matter and sediment, respectively. The overall effect of this is towards decreasing chromium concentrations (dissolved, suspended matter, sediment).

The net result of the processes described is a decrease in the concentrations of chromium in solution, adsorbed onto suspended matter and in the sediment, in a seaward direction. The decrease of chromium concentrations, unlike that of other metals, is in reasonable agreement with the pattern which can theoretically be expected if only the dilution effect (mixing with marine sediment) is considered. This suggests that the effects of other processes counterbalance one another.

3.4. BEHAVIOUR IN AIR

In the atmosphere chromium occurs in the form of aerosols (suspended particles). Consequently, chromium is also found in rainwater and cloud droplets. It is removed from the atmosphere by wet and dry deposition. The particle-size distribution of the chromium-containing aerosol is an important factor in determining the rate at which deposition occurs. Coarse particles are generally removed more rapidly, so that during transport the particle-size distribution shifts to a small diameter.

Chromium aerosol is mainly present in the fine fraction of the aerosol: the mass median diameter, measured at ten locations, is on average 1.1 μm (Milford and Davidson, 1985). Measurements taken in the Netherlands are consistent with this observation (Potma et al., 1986). Chromium aerosol emitted from coal-fired power stations is generally smaller than 1 μm; the particle size of chromium-containing windblown soil dust and of particles derived from arc furnaces in the metallurgical industry is considerably larger: 5-50 μm (Pacyna and Nriagu, 1988). Industrial sources can emit chromium in both the hexavalent and the trivalent state. The available information indicates that combustion-related emissions contain Cr(III); Cr(VI) is emitted, for example, during the chromium-plating process in the electroplating industry (Air Resources Board, 1986).

The deposition velocities for the Dutch situation are estimated at 0.35 $cm.s^{-1}$ (van Jaarsveld and Onderdelinden, 1986), which is equivalent to an average removal rate of about 1.5% per hour. Under conditions pertaining in the Netherlands, the average rate of removal by wet deposition is about 3-4% per hour.

The solubility of the aerosol-bound chromium in water or dilute acid is generally low. Only 1-2% of the chromium collected in open-top rain collectors is soluble in water (Nriagu et al., 1988). The solubility depends on, among other factors, the pH and the oxidation state of the chromium. Cr(VI) occurs as the soluble $HCrO_4^-$ or CrO_4^{2-}; Cr(III) usually exists as the insoluble Cr_2O_3. It is assumed that metallic chromium and Cr(III) are stable in the atmosphere in view of their low reactivity.

In aqueous solutions, Cr(VI) is readily reduced to Cr(III) in the presence of organic material or sulphite, among other substances (Stollenwerk and Grove, 1985b; Vos, 1985). It is assumed that reduction of Cr(VI) to Cr(III) also occurs in the atmosphere (Rühling et al., 1987); no information is available about the rate at which Cr(VI) is reduced.

Measurements of the speciation of chromium bound to aerosol are scarce. Preliminary measurements carried out in California showed that 3 to 8% of the atmospheric chromium is present as Cr(VI) (Air Resources Board, 1986), with an estimated range of 0.01 to 30% because of uncertainties in the measurement technique used. Hexavalent chromium was not demonstrated in aerosol measurements at various locations in Singapore (Goh et al., 1986). However, it should be noted that the detection limit of hexavalent chromium in the latter measurements was 300 $ng.m^{-3}$; for comparison, the annual average total chromium concentration in the Netherlands is estimated at about 3 $ng.m^{-3}$ (Potma et al., 1986). The Cr(III)/Cr(VI) ratio seems to be strongly determined by meteorological conditions. It is assumed that the higher concentration of oxidants (especially ozone) produced by solar radiation can retard the conversion of Cr(VI) to Cr(III), so that the Cr(VI) concentration values would persist relatively longer (De Boer, 1989).

3.5. BEHAVIOUR IN BIOTA

The data in this section are based on those in chapter 5.

Aquatic organisms accumulate chromium only to a limited extent (both in fresh water and sea water). In view of the decreasing concentration of chromium in organisms with increasing trophic level (algae > invertebrates > vertebrates), it is concluded that biomagnification (accumulation through food chains) is of little significance in the aquatic environment.

Terrestrial organisms, too, only accumulate chromium to a limited extent. The concentrations in both earthworms and above-ground parts of crops are many times lower than those in soils, indicating that chromium is not accumulated from soil.

3.6. SUMMARY AND CONCLUSIONS

Chromium occurs in the environment in two oxidation states, Cr(III) and Cr(VI). In terms of effects, Cr(VI) is the most important (see chapter 5). The occurrence of a particular Cr(III)/Cr(VI) distribution depends mainly on the existing redox potential, the pH, and the presence of oxidants and reductants. Cr(VI) is readily reduced to Cr(III) by, for example, organic matter. Powerful oxidants are required for the oxidation of Cr(III) to Cr(VI), such as manganese dioxide in soil and surface water and, for example, ozone in the air.
Cr(VI) always occurs as a negatively charged oxo compound, CrO_4^{2-} or $HCrO_4^-$. It does not form complexes and is adsorbed at relatively low pH values. Cr(III) is a positive ion in an aqueous environment, which can form hydroxides and complexes and is adsorbed at relatively high pH values. Cr(III) compounds are kinetically stable.
Cr(III) is the main species in soil. In surface water the speciation of chromium can very from place to place, and relatively high percentages of Cr(VI) have been observed locally. No conclusive answer can be given regarding the percentage of Cr(VI) in the atmosphere because of analytical problems; it may vary from 0.01 to 30% of the total chromium concentration.
The adsorption of Cr(III) onto soil material is a non-linear process. Distribution coefficients range between 30.10^3 and 300.10^3 $l.kg^{-1}$. Chromium bound to organic matter represents only a small fraction of the total bound chromium in the soil. The distribution coefficients in Dutch surface waters vary from 200.10^3 to 800.10^3 $l.kg^{-1}$. The behaviour of chromium in surface water is mostly similar to that of other heavy metals as regards sedimentation where rivers discharge into freshwater basins and salt water. Release of chromium from sediments depends on resuspension, followed by desorption in the surface water, rather than on adjustment of equilibrium in the sediment followed by diffusion over the sediment-water gradient.
In the atmosphere chromium is bound to the fine fraction of the aerosol. The deposition velocity of chromium is 0.35 $cm.s^{-1}$. The average rate of removal of chromium by dry deposition is about 1.5% per hour, which is estimated to be 3-4% because of wet deposition. On the basis of this, the

average atmospheric residence time under the conditions pertaining in the Netherlands is estimated at about 20 hours.

Accumulation of chromium in biota, both aquatic and terrestrial, is negligible; accumulation through food chains is considered to be unlikely.

4. CONCENTRATIONS AND FLUXES IN THE ENVIRONMENT AND EXPOSURE LEVELS

4.1. SAMPLING AND MEASUREMENT TECHNIQUES

4.1.1. Sampling

The risk of contamination during sampling is great. Because of the large-scale use of chromium, tools and vehicles may release chromium (Davies, 1980), whereas the quantities of chromium to be measured are usually very small. Plastic and polyethylene tools should therefore be used when taking samples, and vehicles must be kept away from the vicinity of the sampling point (Tessier et al., 1984).

Many general procedures and precautions regarding the sampling of chromium and sample pretreatment are similar to those for other heavy metals. The reader is referred to the integrated criteria documents Copper (Slooff et al., 1987) and Cadmium (Ros and Slooff, 1987).

Soil and groundwater

Chromium is usually bound to the solid phase of soils. This phase should therefore not be washed away. The in situ state should be disturbed as little as possible. The sample must be covered to prevent contamination by dust.

When collecting samples of groundwater using porous cups, the cups must be checked for any adsorbed chromium. When the groundwater is sampled via wells, mixing of two or more water types can occur (Scalf et al., 1981). If anaerobic groundwater is abstracted and pipes permeable to air are used, an iron precipitate can form on the walls of the pipes on which chromate can then be adsorbed. The CO_2 pressure changes during groundwater abstraction because of the escape of gas. Iron hydroxide precipitates when the CO_2 level falls. Furthermore, because of a changing redox potential, Cr(III) can oxidize to Cr(VI). Precipitation of iron and oxidation of Cr(III) are prevented when samples are collected in a nitrogen atmosphere (Bom, 1981). Groundwater samples must be preserved as soon as possible after the samples have been obtained. Filtration through a 0.45 μm filter, to collect suspended material, should be carried out in anaerobic conditions.

In the case of speciation analysis, the samples from the saturated zone must immediately be hermetically packed in polyethylene containers. This ensures that the pH, the CO_2 level and the redox potential remain constant. Pollution in the sampling well by clay on which adsorption can occur is also an important source of contamination. There is a provisional practical guideline for soil on the preparation of soil and groundwater for the analysis of heavy metals, including chromium (VPR, 1985).

Surface water and sediments

Samples are collected in polyethylene flasks which have previously been cleaned with a detergent in warm water, with 1:1 nitric acid, and deionized distilled water. For the sampling of sediments, the mud sampler entails the least risk of disturbances of the texture (Siebers and Donze, 1984). Filtration of surface water need not be carried out in anaerobic conditions. Samples must be stored at 4 °C.

Air

The determination of chromium bound to airborne particles is a multistage process. It consists of the sampling of suspended particles on the filter of a sampling device, such as the "High Volume Sampling" method (HVS), applied to chromium (NEN, 1984), or the "Low Volume Sampling" method (Air Resources Board, 1985), and a chemical analysis procedure in which, after pretreatment of the filter sample, quantitative determination of the element concerned is carried out. The inaccuracy of this chemical analysis procedure is generally less than 10%.
The levels thus determined are a fair reflection of the actual Cr concentrations in the air. This is connected with the experimental finding that particles with an aerodynamic diameter of more than about 5 μm are collected with the HVS method with varying efficiency, depending on the meteorological conditions (e.g. wind speed). Consequently, there will be varying underestimation of the actual levels, depending on the proportion of the coarse (> 5 μm) or supercoarse (> several tens of μm) fraction of suspended particles (Van der Meulen, 1987). Part of the chromium emitted by road traffic may be present in the supercoarse particle fraction, resulting in an underestimation of up to, on average, about 20% in the sampling procedure. It is not advisable to take samples with the HVS method within

an area of 50 metres from roads with accelerating traffic. A substantial proportion of the chromium emitted by stationary sources can be present in the coarse particle fraction. It is therefore not recommended to collect suspended particles with the HVS method in the vicinity of such sources. The underestimation involved will be less than 10%.

For speciation analysis it can be useful to take samples with an impinger (Schlager, 1984): additions to the impinger liquid can fix the Cr(III)/Cr(VI) ratio.

4.1.2. Measurement techniques

One of the major problems in the assessment of chromium effects is the lack of adequate methods for determining the species and amounts of chromium.

Several methods are available for the measurement of (total) chromium: atomic absorption spectroscopy (AAS); neutron activation analysis (NAA); X-ray fluorescence; particle induced X-ray emissions (PIXE); colorimetry; differential pulse polarography (DPP); gas and liquid chromatography, and chemiluminescence (EPA, 1984). Table 4.1. gives a few detection limits.

The frequently used AAS analysis can be carried out with NEN 6444 (NEN, 1977). Various methods for the determination of (total) chromium have been reviewed by Griepink (1984).

Separation of Cr(III) and Cr(VI) can be accomplished by (co)precipitation, by selective complexation, e.g. with ammonium pyrrolidine dithiocarbamate (APDC) (Air Resources Board, 1986a), or with 1,5 diphenylcarbazide (DPCI) (Edwards et al., 1985), or by cation and anion exchange. Cr(VI) can also be converted to Cr(III) after prior determination of the Cr(III) fraction (Sjaya et al., 1986), or Cr(III) can be converted to Cr(VI) following the measurement of Cr(VI) (Wai et al., 1987).

Cr(VI) can be directly measured by polarography. An overview of the analytical chemistry of chromium species can be found in Harzdorf (1987).

Table 4.1. *Reported detection limits for chromium in biotic and abiotic environmental samples (Langärd, 1982; Locatelli and Fagioli, 1986)*

Assay procedure	*Detection limit ($\mu g.l^{-1}$)*	*Valency*
Colorimetry	*1.2 - 5*	*III*
Chemiluminescence	*0.03*	*III*
	0.3	*VI*
AAS	*0.05 - 0.2*	
	*0.02 **	
ICP (Ind. Coupled Plasma)	*1 - 5*	
ICP-MS	*0.02*	
DPP	*2*	*VI*
PSA (Potentiom. Stripping)	*5*	*VI*
GLC	*0.1*	*III*

** : $\mu g.m^{-3}$*

4.2. Background concentrations

The average concentration of chromium in soils ranges between 40 mg.kg^{-1} (NAS, 1974) and 100 mg.kg^{-1} (EPA, 1981), and is 125 mg.kg^{-1} in the earth's crust (NAS, 1974). The Cr content of the soil is mainly determined by its concentration in the source material, which varies from traces in old alluvial sands to 4000 mg.kg^{-1} in volcanic rock.

The concentration of chromium in Dutch soils varies widely. The differences can usually be traced back to mineralogical differences (Moura and Kroonenberg, 1988). In areas with little influence of anthropogenic sources, the chromium concentration can range from 40 to 164 mg.kg^{-1} (VTCB, 1986).

In general, the concentration of chromium in groundwater is low (< 1 μg.l^{-1}) (Scheffer and Schachtschnabel, 1982). The average value measured in the Netherlands is 0.7 μg.l^{-1} (Van Duijvenbooden et al., 1985).

The natural chromium concentration in surface water is approximately 1 - 2 μg.l^{-1} (Van Eck et al., 1985; NAS, 1974). Lower natural levels have been reported for salt water: 0.04 - 0.5 μg.l^{-1} (NAS, 1974; Merian, 1984), possibly even 0.4 - 4 μg.l^{-1} (Salomons, IB, pers. comm.). The southern part of the North Sea has a background concentration of 0.7 μg.l^{-1}, of which 0.3 μg.l^{-1} dissolved and 0.4 μg.l^{-1} adsorbed on suspended matter (North Sea Water Quality Plan). The background concentration in sediments in the Netherlands is about 70 mg.kg^{-1} d.w. for both freshwater and marine sediments and polders dating from before 1880 (Salomons, 1981; Van Eck et al., 1985; VTCB, 1986).

An average chromium concentration of approximately 0.3 ng.m^{-3} has been measured in the ambient air of remote areas. The lowest concentrations were observed at the South Pole: 0.005 - 0.013 ng.m^{-3}. The levels are a factor of 6 to 10 higher at the North Pole (0.03 - 0.07 ng.m^{-3}), mainly due to the influence of industrial emissions. In rural areas, the values rarely exceeded 10 ng.m^{-3} (NAS, 1980).

4.3. OCCURRENCE IN SOIL AND GROUNDWATER

The average chromium concentration in soils is 70 mg.kg^{-1} (Bowen, 1979), and varies from traces (uncontaminated soil on rock low in Cr) to 3500 mg.kg^{-1} (serpentine soil) (Aubert and Pinta, 1977). These high values are not found in Dutch soils, the level varying between 11 and 117 mg.kg^{-1} (VTCB, 1986). It is considerably higher in contamination situations (see table 4.6.). This range applies to both natural areas and areas affected by human activity (Edelman, 1984; VTCB, 1986).

Edelman (1984) conducted a study into the relationship between the chromium content and the texture and organic matter class (see table 4.2.).

Table 4.2. *Ranges of measured chromium concentrations in the topsoil (0-10 cm) of areas in the Netherlands, grouped according to texture and organic matter class*

Class	*Chromium content (mg.kg^{-1} d.w.)*
Sandy clay	*11 - 43*
Sandy clay/loam	*33 - 75*
Clay	*75 - 117*
Peaty clay/clayey peat	*66 - 95*
Peat	*16 - 42*

Edelman demonstrated relationships between the Cr concentration and soil characteristics, creating the possibility of making an estimate of background levels. For example, a distinction can be made between the chromium occurring naturally in the soil and that derived from pollution.

Lexmond and Edelman (1986) and De Cleen and Tieleman (1988) showed that for areas with a minimal influence of anthropogenic sources, the Cr concentration is related to the clay (particle size < 2 μm) and silt contents of the soil material. No statistically significant correlation was found between the organic matter content and the Cr concentration. Observed upper limits of the Cr concentration in the top soil of natural areas are compiled in table 4.3., and the average Cr levels in various Dutch soils are presented in table 4.4.

Table 4.3. *Observed upper limits of the chromium concentration in natural areas (VCTB, 1986)*

Soil material	*Chromium content (mg.kg^{-1} d.w.)*
Sand	*56*
clay	*164*
Peat (50% org. matter)	*56*
Peat 100% org. matter, extrap.)	*50*

Table 4.4. *Average chromium concentration in Dutch soils (Van Driel and Smilde, 1981)*

Soil type	*Chromium content (mg.kg^{-1})*	*Range (mg.kg^{-1})*
Clay	*78*	*20 - 130*
Sandy	*26*	*0 - 80*
Bog peat	*63*	*20 - 100*
Moss peat/sand	*20*	*0 - 30*
Loess	*68*	

These findings correspond with the upper limits calculated by Lexmond and Edelman (1986). Analysis of arable soils gave Cr concentrations which differ little, if at all, from those in natural areas (VTCB, 1986), indicating that no (rapid) accumulation occurs. None of the measurements exceeded the upper limits mentioned above. Also, the concentration still acceptable for agricultural soil, 100 mg.kg^{-1}, is rarely exceeded. Considering the proposals for the maximum permissible Cr input to the soil (agricultural soil and maize soil: see chapter 1, tables 1.3. and 1.4.), the (maximum) increase in agricultural areas from the application of sewage sludge is about 0.35 mg.kg^{-1} per year. This increase will fall to about 0.05 mg.kg^{-1}annually in the period 1995-2000 when the proposed measures are implemented.

In the past, heavily contaminated sediment was imported via the Rivers Rhine, Meuse and Scheldt, as is illustrated in tables 4.5. and 4.6.

Table 4.5. Concentrations of chromium in polders reclaimed at different times (Salomons and De Groot, 1977)

Year of reclamation	*Chromium content (mg.kg^{-1})*
1759	*94*
1927	*112*
1957	*406*

Table 4.6. Contaminated soil situations in the Netherlands

Area	*Chromium content (mg.kg^{-1})*	*Reference*
Water meadows (av.)	*277*	*Van Driel and Smilde, 1981*
Broekpolder	*268*	*VROM, 1983*
Kralinger polder	*411*	*VROM, 1983*
Soil removed at Lekkerkerk	*$\leq$ 140*	*Brinkman, 1981*

Few data on Cr concentrations in groundwater are available. The National Groundwater Quality Monitoring Network does not measure chromium. However, it was occasionally measured when the monitoring network was being set up. Van Duijvenbooden et al. (1985) give values of 0.68 μg.l^{-1} for a depth of 10-25 m below ground level with a maximum of 2.4 μg.l^{-1} measured, and 0.87 μg.l^{-1} for depths greater than 25 m below ground level with a maximum of 3.6 μg.l^{-1} measured. In general, groundwater contains $\leq$ 1 μg Cr.l^{-1} (Scheffer and Schachtschnabel, 1982). Significantly higher concentrations were measured in an infiltration area on the Veluwe (Van Duijvenbooden et al., 1981): 1.0 - 5.0 μg.l^{-1}.

River sludge was dumped in the Broekpolder between 1959 and 1976, and its groundwater later contained 3.5 μg Cr.l^{-1} (Kerdijk, 1981).

The average chromium concentration in rainwater is 0.5 μg.l^{-1} (VTCB, 1986), and the expected concentration in groundwater would therefore, in the absence of other sources and losses, be 1.5 μg.l^{-1}, indicating that immobilization in the soil is slight.

4.4. OCCURRENCE IN SURFACE WATER AND SEDIMENTS

4.4.1. Concentrations in surface water and sediments

Concentrations in surface water

The current concentrations of chromium in surface waters and sediments vary, depending on the location. This variation reflects differences in the load situation and in hydrodynamical and (geo)chemical conditions. In the main system of the Dutch State water bodies, the input of chromium via Rhine and Meuse water dominates, while the behaviour of suspended particulates and chromium during passage of the river courses, the large freshwater basins and the freshwater-saltwater mixing zones is also important. In the regional waters, the load situation in particular dominates, especially wastewater effluents and the discharge into the system of water derived largely from the Rhine. The concentration profiles in the State water bodies are summarized in table 4.7. The data are taken from the surface water quality of State waters monitoring network.
In addition to the total chromium concentrations, table 4.7. also shows the concentrations of dissolved chromium (after filtration of particles < 0.45 µm). The Cr concentrations for suspended matter are the quotient of undissolved chromium concentration and the suspended matter content. Average values, and not the concentrations measured in individual samples, were used in the calculation. As a result, the values given are only an indication. The annual average concentrations of total and dissolved chromium are presented in table 4.8. for the year 1987.

Table 4.7. Cr concentrations in the State water bodies (in µg.l^{-1}, total and dissolved), and Cr concentrations in suspended matter (mg.kg^{-1} d.w.)

Location	*1974 - 1976*			*1979 - 1981*			*1984*		*1986*
	Tot. water	*Dis-solved*	*Susp. mat.*	*Tot. water*	*Dis-solved*	*Susp. mat.*	*Tot. water*	*Dis-solved*	*Susp. mat.*
Rhine									
Lobith	*52*	*10*	*1100*	*19*	*3.9*	*380*	*8.4*	*1.1*	*190*
Kampen	*29*	*8.2*	*690*	*14*	*3.8*	*350*	*7.1*	*0.8*	*190*
Lake Ketel	*14*	*5.1*	*720*	*8.0*	*2.3*	*380*	*4.0*	*0.6*	*180*
Lake IJssel	*3.6*	*1.6*	*80*				*2.5*	*0.5*	*65*
Vuren	*33*	*11*	*790*	*23*	*4.8*	*590*	*8.3*	*0.8*	*180*
Maassluis	*19*	*4.6*	*600*	*14*	*2.5*	*520*	*5.1*	*0.7*	*270*
Meuse									
Eysden	*13*	*3.0*	*340*	*13*	*2.4*	*210*	*8.5*	*2.1*	*220*
Keizersveer	*9.4*	*2.0*	*340*	*6.1*	*1.4*	*200*	*3.5*	*0.8*	*190*
Rhine/Meuse									
Haringvliet									
- bridge	*10*	*3.3*	*850*	*7.0*	*2.5*	*450*	*2.7*	*0.7*	*270*
- lock	*5.5*	*2.4*	*520*	*5.0*	*1.9*	*370*	*2.7*	*0.7*	*210*

The chromium levels have fallen over the past decade, by about 85% in the Rhine and about 35% in the Meuse. The 90th percentile for State waters is < 25 µg.l^{-1}.

Table 4.8. Chromium concentrations in the State water bodies (in µg.l^{-1}, total and dissolved)

Location	*Dissolved*	*Total*	*Location*	*Dissolved*	*Total*
Lobith	*0.6*	*7.5*	*Scheldt (border)*	*0.6*	*19.3*
Kampen	*0.6*	*7.1*	*Eysden*	*2.0*	*9.9*
Lake Ketel	*0.6*	*4.8*	*Keizersveer*	*0.7*	*7.3*
Lake IJssel	*0.4*	*1.5*	*Haringvliet-bridge*	*0.7*	*3.7*
Vuren	*0.5*	*10.9*	*Haringvliet-lock*	*0.7*	*3.4*
Nieuwe Waterweg	*0.6*	*4.5*			
North Sea (coast)	*0.2*	*4 - 15*	*North sea (central)*	*0.1*	*0.5*
Wadden Sea	*0.2*	*3 - 11*			

The chromium concentrations in regional waters are significantly lower than those in the State water bodies: 1 to 6 µg.l^{-1} approximately; according to DBW/RIZA, the 90th percentile is < 12 µg.l^{-1}. Sharply elevated levels have

occasionally been reported, sometimes up to > 100 $\mu g.l^{-1}$ (CUWVO, 1987; Zuid- Holland, 1989; WL, 1987). In 1985 and 1986 only one case which exceeded the basic quality (50 $\mu g.l^{-1}$) was reported. The water quality data on regional waters, which are based on the CUWVO inventory, show that the average chromium concentrations in the eastern and central sandy areas range from 0.5 to 3 $\mu g.l^{-1}$. Slightly higher chromium levels have been found in Limburg and eastern North Brabant, with average values ranging between 4 and 5 $\mu g.l^{-1}$. The highest concentrations have been reported for the clay/peat areas, up to 6-7 $\mu g.l^{-1}$.
Information about the occurrence of Cr(III) and Cr(VI) species in surface waters is limited.

Concentrations in sediments

Analysis of Cr sediment concentrations in State waters (period 1980-1985; converted to standard soil) gives the picture outlined in table 4.9. (WL, 1985). The values measured for the chromium content of a large number of sediments show that the majority lie in the 80 to 400 $mg.kg^{-1}$ range, with a few peaks of up to about 800 $mg.kg^{-1}$ (Turkstra, 1988). Chromium concentrations in the range of 20 to 185 $mg.kg^{-1}$ have been found in Dutch sediments since 1985 (10th and 90th percentile; not converted to standard soil).

Table 4.9. Chromium concentrations in Dutch sediments, in $mg.kg^{-1}$ d.w.

Location	*Percentile* *10*	 *50*	 *90*
Rhine/Rhine branches	*25*	*122*	*280*
Meuse/Meuse branches	*12*	*68*	*170*
Rotterdam harbours	*92*	*181*	*292*
Lake IJssel	*4*	*23*	*89*
Holl. IJssel River	*30*	*149*	*240*
State water, fresh	*14*	*85*	*265*
State water, salt	*17*	*78*	*120*
State water '85-'87	*20*	*90*	*185*
as above, non-State water	*11*		*68*

The Cr levels in sediments follow, with some delay, the downward trend of the concentrations in surface waters. Table 4.10. summarizes the available information on the trend in sediments (Salomons, 1981; WL, 1985, 1988; DG, 1988; Turkstra, 1988; Misdorp and Duijts, 1988).

Table 4.10. *Development of chromium levels in sediments (in mg.kg^{-1}, with 50% of particles < 16 μm)*

Year	*Rhine (¹)*	*Meuse (²)*	*Haringvliet*		*Lake Ketel*	*Lake IJssel*	*Scheldt*	*Wadden Sea*	*North Sea (coast)*
			bridge	*/lock*					
1922	*110*								
1933						*88*			
1958	*640*	*215*							
1962					*572*				
1970	*790*	*325*	*408*					*116*	
1971	*814*	*304*	*567*	*306*					
1972	*908*		*563*	*326*	*680*				
1973	*873*		*479*	*267*					
1974					*460*	*106*	*380*		
1975	*829*	*330*	*605*	*376*					
1977	*850*	*255*	*489*	*397*	*485*	*93*		*124*	
1979							*290*		*95-*
1981								*133*	*175*
1983	*815*	*380*	*274*	*313*	*274*				
1986									*73-*
1987								*98*	*175*

¹) *Nieuwe Merwede;* ²) *Amer*

Information about chromium concentrations in the sediments of regional water bodies will become available now that the sediment quality is being catalogued in view of their contamination and spoil disposal problems. The survey taken in North Brabant (Noord-Brabant, 1987) gives the picture outlined in table 4.11.

Table 4.11. Results of survey of sediment quality in North Brabant

	Chromium content $mg.kg^{-1}$	Number of observations n	 %
	0 - 10	76	28
	10 - 20	58	22
	20 - 30	37	14
	30 - 40	19	7
	40 - 50	10	4
Total	0 - 50	200	75
	50 - 100	29	11
	100 - 200	18	7
	200 - 500	11	4
	500 - 1000	5	2
	1000 - 2500	3	1
	2500 - 5000	1	-
Total		267	100

The inventories show that the average Cr concentration in sediments is about 15 - 30 $mg.kg^{-1}$ with a range of 5 to 100-200 $mg.kg^{-1}$ (50th percentile in State water is about 90 $\mu g.l^{-1}$ and in non-State water about 28 $\mu g.l^{-1}$). This is comparable to the Cr levels in terrestrial soils: 11 - 120 $mg.kg^{-1}$ (Edelman, 1984). The recent survey in South Holland gives more or less the same picture as that observed in North Brabant (Zuid-Holland, 1989). The chromium level is less than 100 $mg.kg^{-1}$ in 88% of the cases, and below 600 $mg.kg^{-1}$ in all cases (after standardization of clay (diam. < 2 μm)/organic matter levels).

4.4.2. Input to the surface water system

Transboundary transport

The largest source of chromium to the surface water system is the transboundary transport by rivers. It was 633 tonnes in 1986, of which 70-80% adsorbed on suspended particulates. A breakdown of this figure according to supply route, and the development in time are given in table 4.12. The term "Other" includes, for example, rivers such as the Swalm, Roer, Niers and Vecht. The estimates of their chromium loads are uncertain (WL, 1987).

Table 4.12. Transboundary chromium transport by rivers, in tonnes per year

	1970	*1979-1981*	*1984-1986*
Rhine	*ca 4000*	*1350*	*563*
Meuse	*ca 300*	*220*	*88*
Scheldt		*100*	
Eems		*10*	
Other		*ca 46*	

Atmospheric deposition

The total chromium input to surface waters by atmospheric (dry and wet) deposition was < 2 tonnes in 1986 (CUWVO, 1987) (see also chapter 2). The distribution between State and regional water bodies was 3:1.

Direct industrial discharges and sewage treatment plants (STP)

The total chromium input to the surface water from discharges of industrial and domestic waste waters (after passing through STPs) was 93 tonnes in 1986. The National Water Quality Plan gives a breakdown and the expected development (VROM/V&W, 1986), see table 4.13. A breakdown of the load for State water bodies (chiefly Rhine and Meuse) and non-State water bodies is given in table 4.14. for the 1985/1986 situation. The information given in chapter 2 was used for most of the sources. The breakdown is based on information from the National Water Quality Plan and CBS data (CBS, 1987). The estimates of the inputs from runoff, seepage and discharge water (drainage of regional water bodies into State water, including transboundary rivulets, etc.) are taken from WL data (WL, 1987).

Table 4.13. *Chromium input to State water bodies from discharges of industrial and domestic waste waters, in tonnes per year*

	1980	*1985*	*1990*
Direct industrial discharges:	*96*	*81*	*18*
of which:			
- Tidal rivers	*81.7*		
- Upper rivers	*0.7*		
- Meuse	*1.1*		
- North Sea Canal/A'dam-Rhine Canal	*6.8*		
- Dollard and Wadden Sea	*1.0*		
- Southern Delta waters	*5.0*		
Municipal waste water (after STP)	*16*	*12*	*4*
Total	*112*	*93*	*22*

Table 4.14. *Chromium input to the surface water system '85/'86 (tonnes per year)*

Source	*Total*	*State water*	*Regional*
Atmospheric deposition	*2*	*1.5*	*0.5*
Runoff	*0.7*		*0.6*
STP effluents	*11*	*5*	*6*
Direct industrial discharges	*82*	*78*	*4*
Seepage/percolation	*6*		*6*
Discharge water	*41*	*41*	
Rhine/Meuse	*633*	*633*	
Other rivers	*110*	*110*	
Total	*886*	*869*	*11*

A summary of the chromium input to the North Sea (Dutch part of the continental shelf), which was drawn up for the North Sea Water Quality Plan, shows that, with unchanged policy, a reduction of about 1000 tonnes per year is expected in 1990 compared with 1980. In 1990, river influxes of chromium to the North Sea will account for 90% of the total load (VROM/V&W, 1985).

4.4.3. Dispersion and risk areas

Risk areas in connection with chromium in the surface water system are especially those areas where suspended materials sediment. In the State water bodies these are the water meadows, Biesbosch/Hollandsch Diep/Haringvliet, Lake Ketel/Lake IJssel, estuaries and the Tidal rivers area. Where sources discharge waste water, local sedimentation areas are important: harbour basins, stagnant water bodies and dead corners. For the North Sea these are the areas directly influenced by wastewater effluents and rivers discharging into the sea, for example, the coastal region near the Nieuwe Waterweg, as well as the sedimentation area north of the Frisian islands and the Wadden Sea itself.

Several attempts have been made to draw up zero mass balances for the Rhine/Meuse system (among others, Salomons, 1981; Dijkzeul, 1982; IMP 1985-1989). In none of the cases did input equal output, and the balance sheets had deviations of several tens of percent. Furthermore, there is a tendency towards decreasing retention of chromium with decreasing chromium input. The retention of metals in the large basins plays an important part in the dispersion of metals in, and their transport through, the Netherlands. The ZMAS study (ZMAS, 1984) gives the following contributing factors (for 1977-1978): Hollandsch Diep/Haringvliet: a total of 79% retained, 30% dissolved Cr, 84% adsorbed Cr; Lake Ketel/Lake IJssel: a total of 80% retained, 87% dissolved Cr, 71% adsorbed Cr. The amounts of chromium accumulated over this period were estimed at about 850 tonnes per year in Hollandsch Diep/Haringvliet, and 190 tonnes per year in Lake Ketel/Lake IJssel.

An indicative balance sheet has been drawn up for 1985 (table 4.15.). The ingoing and outgoing loads are based on concentrations measured in the period 1984-1986 (table 4.7.). Using these levels, chromium loads have been calculated on the basis of the water budget in an average year. The loads used for effluents and removal in dredged spoil are rough estimates. Proportionality has provisionally been assumed for the load in spoil. The amount of chromium removed via the North Sea Canal has been disregarded, as well as the effluents into the Amsterdam-Rhine Canal and the North Sea Canal.

The balance sheet for 1980 shows that the Lake Ketel/Lake IJssel basin retained 69% and the Hollandsch Diep/Haringvliet basin 64% of the chromium entering them. These percentages are lower than those of ZMAS (1984), possibly as a result of the changed load situation. Based on the chromium concentrations in inflowing and outflowing water, the basins retained less chromium in 1985 than in 1980. The development since 1977/1978 makes it likely that with the fall in chromium levels in Rhine water and, to a lesser extent, also Meuse water, the accumulation of chromium in freshwater basins is decreasing not only in absolute but also in relative terms.

Table 4.15. Indicative chromium balance sheet, 1985 base year

Input/removal	*Chromium load (tonnes per year)* *constituent flows*	*total*	*% of input*
Input			
Rhine	*580*		
Meuse	*75*		
Effluents, total:	*78*		
Discharge from rivulets into Meuse	*66*		
Atmospheric deposition	*1*		
Total input		*800*	
Transport to sea			
Haringvliet	*62*		
Nieuwe Waterweg	*242*		
Lake IJssel	*28*		
Total river transport to sea		*332*	*42*
Total removal in dredged spoil			
(land locations and sea)		*320*	*40*
Accumulation			
(Lake Ketel, Lake IJssel)			
Input via IJssel River	*79*		
Removal via Lake IJssel Dam	*28*		
Total		*51*	*6*
(Holl. Diep/Haringvliet)			
Input	*179*		
Removal	*82*		
Total		*97*	*12*
Total removal + accumulation		*800*	*100%*

4.4.4. Expectations

In view of the development of the Cr concentrations in Rhine water and the current treatment of effluents, it may be expected that the Cr levels in the greater part of the surface water and deposited sediments in the Netherlands will fall still further. However, this is not certain for the Meuse and the water bodies fed by this river.

4.5. OCCURRENCE IN AIR

4.5.1. Concentrations in outdoor air

Regional background

Little is known about the occurrence of chromium in general and Cr(VI) in particular. Measurements at 5 locations in the Netherlands in 1982/83 (Thijsse and Huygen, 1985) showed that the regional background concentration in the Netherlands ranged from 2 to 5 $ng.m^{-3}$ (see table 4.16.). It is not known by how much these levels have fallen during the past few years as a result of emission reductions at home and abroad. The proportion of Cr(VI) is also not known.

Table 4.16. Concentration of chromium in Dutch outdoor air (1982/1983)

Location	*Concentration* ($ng.m^{-3}$)
Witteveen	*2.0*
Rekken	*4.3*
Bilthoven	*2.5*
Vlaardingen	*4.7*
Biest-Houtakker	*2.1*

The researchers estimated that approximately 25% of the chromium originated from windblown soil dust. As part of the same project, the chromium concentrations in Dutch ambient air have been calculated for the period 1982/1983 (assuming a Dutch emission of about 5 tonnes of chromium annually) (Van Jaarsveld and Onderdelinden, 1986). The agreement between the measured and calculated concentrations is good. The calculated concentrations, averaged over 15x15 kilometres, are given in figure 4.1. The average calculated concentration across the Netherlands is 2.7 $ng.m^{-3}$.

Whereas at that time the contribution from Dutch sources to the chromium concentration in the Netherlands was as high as 36%, it has now fallen to about 10% because of emission reductions in the Netherlands (see also 4.7.).
In Belgian cities near the border, average values of 20 ng.m^{-3} (Antwerp) and 140 ng.m^{-3} (Genk) were measured in 1985 as compared with a regional Belgian background level of about 10 ng.m^{-3} (IHE, 1986).

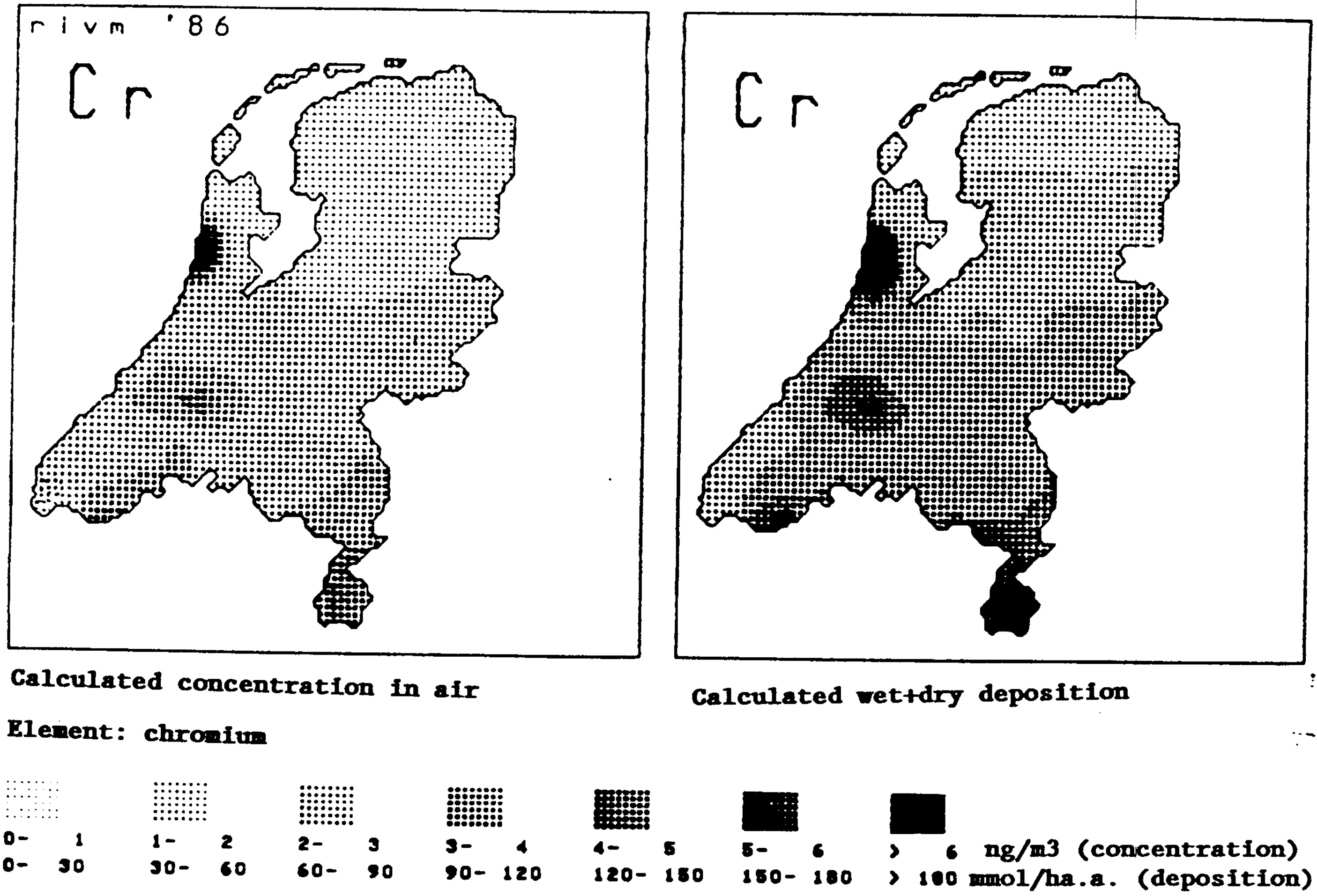


Figure 4.1. *Calculated chromium concentration in air (l) and calculated wet + dry deposition (r) for 1982/1983. The source strength of the point sources, as shown in the west and centre of the country, has meanwhile decreased*

Local
It has been reported in the literature (Nriagu and Nieboer, 1988; Air Resources Board, 1986b) that the concentration of chromium in the air of cities is often a factor of 2 to 4 higher than the regional background

level. The emission of chromium by local industries will obviously contribute to the chromium levels in the air around these sources. For example, the average atmospheric concentrations determined at 2 sampling points in Liege (Belgium) in 1985 were 30 and 170 $ng.m^{-3}$, respectively (IHE, 1986).

Detailed emission data for an accurate calculation are not available. It is certain that part of the chromium is emitted as Cr(VI). In view of the short residence time (at an average wind speed of 5 $m.s^{-1}$, a Cr particle is carried a distance of about 1.5 kilometres within 5 minutes), only a small fraction of any chromium present will have been converted to Cr(III). In the case of a Cr(VI) emitter, the proportion of Cr(VI) can amount to several tens of percent.

An additional concentration of about 5 $ng.m^{-3}$ (Cr(VI)) has been calculated in the vicinity ($\leq$ 50 m) of low sources, such as small chromium-plating establishments.

4.5.2. Deposition

On the basis of the model calculations described above, the deposition rate of chromium in the Netherlands, averaged over 5x5 kilometres, has been calculated (see figure 4.1.). The calculated wet deposition rate is 1.7 $g.ha^{-1}$ per year, and the calculated dry deposition 1.3 $g.ha^{-1}$ per year. The calculated wet deposition differs slightly from the measured value (the latter was fairly constant between 1982 and 1988, viz. 0.01 $\mu mol.l^{-1}$ or 3.9 $g.ha^{-1}$ per year). This can be partly explained by the use of open-top rain collectors and the fact that the measured Cr concentration was approximately the same as the minimum level detectable of 0.01 $\mu mol.l^{-1}$. Because of the method used, a large proportion of the dry deposition was also included. Nevertheless, it is assumed that a total of about 13 tonnes of chromium is deposited annually on Dutch soil, of which around 8.5 tonnes originate abroad (see also 4.7.).

4.5.3. Concentration in indoor air

Nonoccupational setting

Significantly higher concentrations can be expected in dwellings with smokers. Cigarettes contain 0.24-15 $mg.kg^{-1}$ (WHO, 1988) (average ca 4 $mg.kg^{-1}$), which means that 0.06 tonne of chromium is emitted annually in

Dutch homes. On the basis of measurements of benzene and cadmium in dwellings, where concentrations of 100 $\mu g.m^{-3}$ (Slooff, 1987; WHO, 1988) and 0.01-0.1 $\mu g.m^{-3}$ (Ros and Slooff, 1987), respectively, have been found as a result of smoking, it can be expected that the chromium concentrations in these dwellings (with an emission which is a factor of 130 [2] lower [higher] than for benzene [cadmium]) can be of the order of 1000 [20-200] $ng.m^{-3}$, approximately 10 to 400 times higher than in the Dutch atmosphere.

Occupational setting

In the workplace, the labour inspectorate expects problems with chromium compounds, especially in the small establishments of the electroplating industry, and during the welding of alloy steel and zinc chromate-treated steel (Jochems, 1986). A few measured concentrations are presented in table 4.17.

Table 4.17. Chromium concentrations in the workplace

Type of activity		*Year*	*Type of measurement*	*Cr(VI) x10^3 ng.m^{-3}*	*Cr(tot.) x10^3 ng.m^{-3}*
Electroplating industry		*1978*	*stationary*	*1 - 9*	
Glass industry		*1979*	*stationary*	*0 - 6*	
Pigment industry		*1982*	*PAS*	*10 - 40*	
Welding of	*chromium plate*	*1976*	*PAS*		*200 - 1100*
	stainless steel	*1979*	*PAS*	*90 - 120*	*340 - 600*
	stainless steel	*1980*	*PAS*	*30*	*210*
	strips	*1985*	*PAS*	*5 - 39*	*45 - 83*
	primer	*1981*	*?*	*< 1 - 3*	*2 - 4*
Cutting of	*steel*	*1978*	*PAS*	*70 - 180*	*560 - 890*
	Iconel	*1978*	*PAS*	*730 - 2700*	*930 - 4700*

During welding operations, welding fumes contained, on average, 4.7% Cr by weight and 1.2% Cr(VI) by weight. From a TNO report (IMG-TNO, 1983), commissioned by DGA, the following relevant passages in this context can be quoted:

"The fumes from welding with coated stainless-steel electrodes were found to contain from 0.5% to 2.7% chromium. Fifty to 90% of this was soluble, resulting in 0.3% to 1.9% Cr(VI) in the welding fumes. Hexavalent chromium occurs almost exclusively in the soluble form and the other chromium species in the insoluble form."

"Assuming that the welding fumes contain 2.5% Cr(VI), this means that the MAC value of 50 $\mu g.m^{-3}$ is exceeded if the total welding fume concentration were more than 2 $mg.m^{-3}$. This is a value which is usually exceeded when welding with coated electrodes. It was always exceeded in the cases investigated by us:

- appliances factory: welding fume concentration 6 - 30 $mg.m^{-3}$
  Cr(VI) concentration 25 - 150 $\mu g.m^{-3}$
- shipyard : welding fume concentration 5 - 11 $mg.m^{-3}$
  Cr(VI) concentration 25 - 210 $\mu g.m^{-3}$

In none of the cases was the MAC for total chromium (500 $\mu g.m^{-3}$) exceeded."

4.6. OCCURRENCE IN FOOD AND DRINKING WATER

The chromium content of most foods is so low that its determination presents a problem. Consequently, many literature data on chromium in food are unreliable. Only a few foodstuffs contain large amounts of chromium. Vegetables generally contain chromium in the range of <10 to 1100 $\mu g.kg^{-1}$, the highest levels often being found in peas and beans (MAFF, 1985a).

In the Netherlands, an investigation into the daily intake of chromium from the diet has not yet been completed. However, the concentrations in a few foodstuffs have been measured (table 4.18.).

Table 4.18. *Chromium concentrations (μg.kg^{-1}) in foods in the Netherlands (Haring, 1984; Staarink and Hakkenbrak, 1987; Ellen et al., 1989)*

Food	*Chromium content*	
	Range	*Median*
Lettuce	*100 - 11000*	*1000*
Endive	*100 - 19000*	*1300*
Purslane	*100 - 500*	*900*
Celery	*150 - 750*	*480*
String beans	*< 800*	*110*
French beans	*< 230*	*130*
Leek	*< 640*	*290*
Tomato	*< 800*	*170*
Radish	*< 600*	*160*
Meat products	*0 - 4x10^{-7}*	*1x10^{-7}*
Eel	*< 300*	*40*
Drinking water	*< 1*	
Baby and infant food	*< 320*	*< 50*
*Ox kidneys **	*< 10 - 1040*	*< 10*
*Pig's kidneys **	*< 10 - 270*	*10 - 20*
*Sheep's kidneys **	*< 10 - 110*	*< 10*
Chicken kidneys	*< 10 - 20*	*< 10*

** fresh product*

Total diet studies carried out in England during the years 1976-1978 showed that the average daily chromium intake was 136 μg (MAFF, 1985a).

There are large differences in the results of studies into the Cr intake from the diet (table 4.19.). Interpretation of these differences is difficult because standard reference material or suitable procedures were not always used in the analyses and, moreover, different methods were employed (WHO, 1988).

Table 4.19. *Daily intake of chromium (µg) from food and water (WHO, 1988)*

Country	*Chromium intake*		*Comment*	*Reference*
	range	*av.*		
Finland		*29*		*AAS (1980)*
Canada	*136- 282*	*189*		*NHW (1980)*
West Germany	*11- 195*	*62*	*24-hour diet*	*Schelenz (1977)*
Japan	*202-1710*	*723*	*city*	*Murakami et al.*
	>180-1190	*943*	*rural areas*	*(1965)*
New Zealand	*39- 190*	*81*	*24-hour diet*	*Guthrie (1973)*
England	*80- 107*			*Smart and Sherlock (1985)*
		134	*24-hour diet*	*MAFF (1985b)*
USA	*5- 115*	*52*	*24-hour diet*	*Levine et al. (1968)*
USA	*25- 224*	*78*	*24-hour diet*	*Kampulainen et al. (1979)*
USSR	*88- 126*		*children*	*Goncharov (1968)*
Belgium	*<0.001-5200*	*370*	*24-hour diet*	*Buchet et al. (1983)*

The average intake in the Netherlands is assumed to be about 100 µg Cr per day, with a range of 50 to 200 µg Cr per day.

4.7. CHROMIUM BALANCE SHEET FOR THE NETHERLANDS

The balance sheet given in figure 4.2. has been constructed from the material flows mentioned previously, supplemented with estimates. Its aim is to sketch a consistent picture of the material flows for chromium in the Dutch environment. The two sides of the balance sheet have been equalized. The precise magnitude of the separate balance items has been subordinated to this.

A multicompartmental box model (Singh and Van de Meent, 1989) was used in drawing up the balance sheet. The balance sheet is based on a highly schematized representation of the environment. In this schematization the air above the Netherlands is regarded as a mixed system. In addition, three water systems ("Lake IJssel", "Haringvliet/Rotterdam", "North Sea") and three soil systems ("agricultural soil", "waste dumps", "other soil") are distinguished. In this context, "North Sea" refers to a coastal strip about 50 km wide. The characteristic parameters are given in table 4.20.

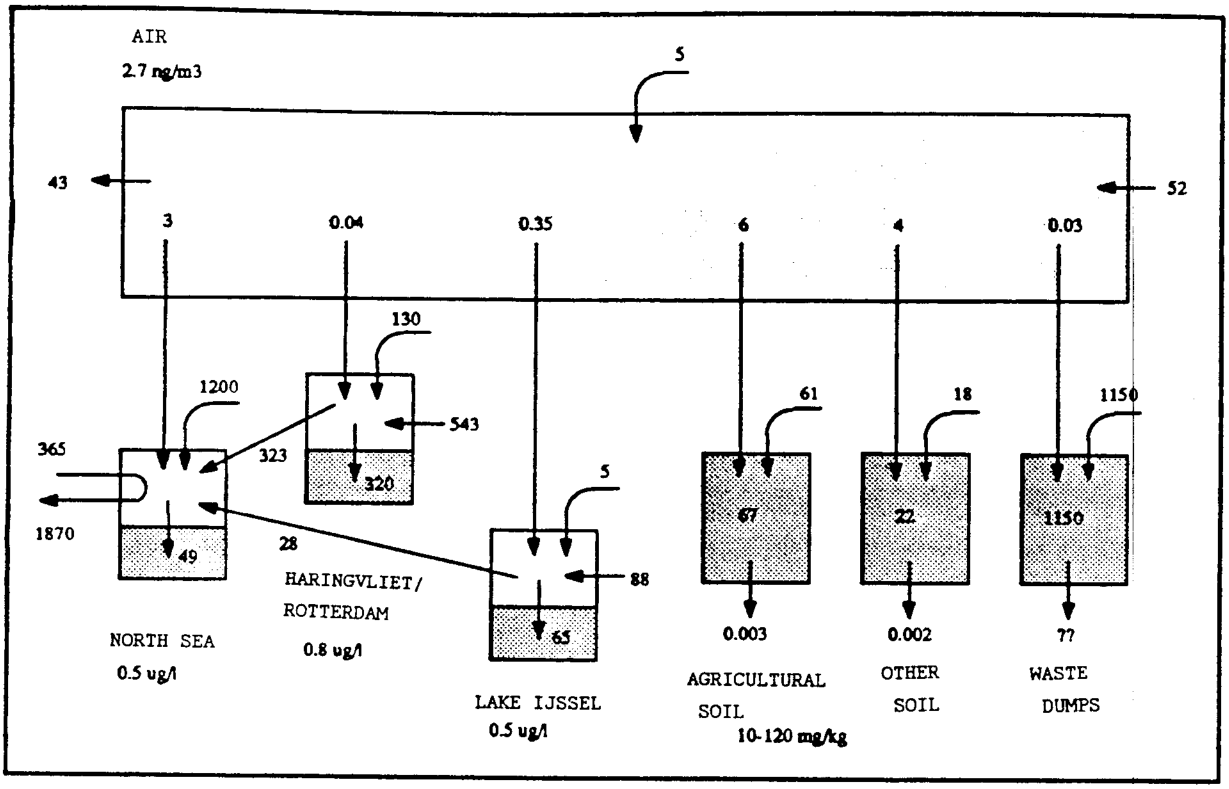


Figure 4.2. *Chromium balance sheet for the Netherlands (in tonnes of Cr per year)*

Table 4.20. *Scheme of the Dutch environment, as a basis for the chromium balance sheet for the Netherlands*

	Air	Lake Ketel/ Lake IJssel	Haringv. R'dam	Coastal water	Agric. soil	Other soil	Waste dumps
Surface area[km^2]	45750	1200	150	10000	20600	13700	100
Height/Depth [m]	800	4	7	10	0.2	0.05	1
Residence time[d]	0.8	130	5	30	-	-	-
Flow [$m^3.s^{-1}$]	5E+08	400	2250	4E+04	-	-	-
Sedimentation [$tonnes.yr^{-1}$]	-	1000	1400	50			
Percolation[$mm.yr^{-1}$]	-	-	-	-	200	200	??
Kd value [$l.kg^{-1}$]	-	1.5E+05	3.0E+05	2.0E+05	1.0E+05	1.0E+05	??

Air

At an average atmospheric Cr concentration of 2.7 $ng.m^{-3}$ and a total deposition velocity of 0.35 $cm.s^{-1}$ (see 4.5.), 13.4 tonnes of chromium are calculated to be deposited annually on the Netherlands (10 tonnes on land, 0.4 tonne in the fresh surface waters and 3 tonnes in the salt water). At an annual emission of 5 tonnes of chromium in the Netherlands, it follows that the net transboundary transport is -8.5 tonnes per year. The associated gross flows have been estimated as follows: exports of about 43 tonnes have been calculated from the average chromium concentration in air and the residence time of air over the Netherlands. The associated imports are then around 52 tonnes per year, corresponding to an average concentration of 3.2 $ng.m^{-3}$ in the air at our frontiers. It should be pointed out here that the atmospheric concentrations mentioned are representative of those at ground level, and that the average concentrations at mixing height are lower. The calculated flows are therefore overestimates. It is estimated that no more than about 90% of the chromium in the air over the Netherlands originates abroad.

Water

The chromium balance sheet for water is based on a long-term average water and sediment budget (DHV, 1988). The loads mentioned here are virtually the same as those on the indicative balance sheet in table 4.15. Using the average levels of chromium in Rhine and Meuse water mentioned previously, the amount imported is 630 tonnes, of which 88 tonnes enter the Lake Ketel/ Lake IJssel system and 543 tonnes the Haringvliet and the Rotterdam harbour area. An additonal 5 and 100 tonnes of chromium per year respectively, are emitted in these two systems. Sixty-five and 320 tonnes of chromium per year respectively, are retained as a result of sedimentation. This is consistent with the concentrations, distribution coefficients and net sedimentation rates reported for these basins. Note that 250 of the 320 tonnes of chromium sedimented in the Haringvliet and the Rotterdam harbours are removed again by dredging operations. This is not shown in figure 4.2. The chromium transported to the North Sea is the closing entry and totals about 350 tonnes per year. This is not much compared with the 1200 tonnes of chromium discharged annually into the coastal waters. A rough estimate of the mass balance for chromium in the coastal waters has been made on the basis of an assumed residence time of 30 days for water off the coast. The associated water flow from the south supplies about 365 tonnes of chromium annually. Atmospheric deposition (3 tonnes per year on the surface area concerned) is negligible. The net result is that the chromium concentration in sea water off the Dutch coast is approximately doubled and that a chromium load of around 1870 tonnes per year is transported northwards (Wadden Sea, German Bight; see figure 4.2.).

Soil

Because of the high K_d values, it must be supposed that leaching and runoff of chromium from the mixed top layer of the soil are negligible. Using a concentration of 10-120 mg.kg^{-1} and a K_d value of 10^5 l.kg^{-1}, this is estimated to be only a few kilograms for the Dutch soil as a whole. The accumulation on agricultural soil is 67 tonnes per year. At a mixing depth of 20 cm, this corresponds to an annual increase of the chromium content by about 10 μg.kg^{-1}. For the other soils the accumulation is 22 tonnes per year, corresponding to an increase of 20 μg.kg^{-1}.$year^{-1}$ (assumed mixing depth is 5 cm). The input of chromium to the environment from the dumping of waste is 1150 tonnes per year, making this the second largest chromium flow.

4.8. EXPOSURE LEVELS

4.8.1. Man

With respect to man, from the point of view of the type of effect caused by chromium (see chaper 5), a distinction should be made between exposure by inhalation (Cr(VI) - carcinogenic effects; Cr(III) - no carcinogenic effects) and oral exposure (no carcinogenic effects).

The daily dietary intake has been estimated at 100 (range 50-200) μg Cr. The chromium in food is present mainly in organically bound form, for which a fractional absorption value of 25% is assumed (see chapter 5). The average amount of chromium absorbed from the diet is therefore estimated to be 25 μg per day.

The background pollution load to which the Dutch population is exposed by inhalation is about 2-5 ng.mg^{-1}. The percentage of Cr(VI) in ambient air can vary between 0.01 and 30%, corresponding with 0.0002-0.0005 and 0.6-1.5 ng Cr(VI).m^{-3} respectively. Higher Cr(VI) concentrations can occur near Cr(VI)-emitting sources. These sources are metal production (ca 150 establishments), paint application (over 100 establishments) and Cr compounds-producing firms (2). They are generally small enterprises, scattered across the country, with relatively small Cr emissions. The emission of Cr(VI) will on average be about 2 kg per year, which, according to calculations, results in a contribution to the concentration of about 5 ng.m^{-3} at 50 m from the source. The highest emission [as Cr(VI)] is estimated at no more than 50 kg per year (see chapter 2); in this case the

concentration contribution at 500 m from the source will be a few ng.m^{-3} at most. Consequently, the exposure level to which the general population is exposed locally will not exceed 5 ng Cr(VI).m^{-3}; the size of this risk group is estimated to be between 5,000 and 50,000 persons.
With respect to Cr(III), cigarette smoke is a major source of Cr(III). The total Cr concentration in smoky rooms is estimated at 20-200 µg.m^{-3}. Cigarette tobacco from the USA contains between 240 and 6300 µg.kg^{-1}, corresponding to about 4 (range 0.2-6) µg.kg^{-1} per cigarette. If it is assumed that chromium is bound to the same aerosol fraction as cadmium and using the same fractional absorption percentage for the two metals, then the daily amount of chromium absorbed after inhalation by an average smoker (10 cigarettes per day) is 0.1-2.7 µg.

4.8.2. Ecosystems

With respect to aquatic organisms, the concentrations in water are relevant. The total chromium concentrations in the State water bodies usually range from 1 to 10 µg.l^{-1}, corresponding to 0.2-2 µg.l^{-1} dissolved Cr. The exposure level in regional water bodies is generally lower, but higher levels are occasionally observed, sometimes up to > 100 µg.l^{-1} total Cr. The exposure levels in the water off the North Sea coast and of the Wadden Sea lie around 0.2 µg.l^{-1} dissolved Cr, those in the central part of the North Sea around 0.1 µg.l^{-1}.
The exposure level for terrestrial organisms varies widely from species to species, depending on, among other factors, living and feeding habits, build and soil parameters.

4.9. SUMMARY AND CONCLUSIONS

A summary of ranges of average chromium levels in the Dutch environment and in the diet is given in table 4.21.

Table 4.21. Summary of ranges of average chromium concentrations in soil, water, air and diet in the Netherlands, as well as a few background levels

Soil	
range of background levels	40 - 164 mg.kg^{-1}
clay (av)	78 mg.kg^{-1}
sand (av)	26 mg.kg^{-1}
Water	
- Fresh	
background level	1 - 2 µg.l^{-1}
surface water (1987)	1 - 10 µg.l^{-1}
sediments	20 - 185 mg.kg^{-1}
- Salt	
background level	0.5 µg.l^{-1}
North Sea coast	4 - 15 µg.l^{-1}
sediments - coastal area	73 - 175 mg.kg^{-1}
- southern part of North Sea	40 - 70 mg.kg^{-1}
- Groundwater	
national	0.7 - 2.4 µg.l^{-1}
local	1 - 5 µg.l^{-1}
Air	
national	2 - 5 ng.m^{-3}
near sources [as Cr(VI)]	< 10 ng.m^{-3}
indoor air, smoky rooms	20 - 200 ng.m^{-3}
wet deposition	0.1 µmol.l^{-1}
Diet *	
daily food parcel (incl. drinking water)	50 - 200 µg

* Estimate based on foreign data

There are sufficient analytical methods available for measuring total chromium concentrations, but methods for determining the forms of occurrence of chromium, in this case Cr(III) or Cr(VI), need to be further developed.

The occurrence of chromium in soils is characterized by a large variation in the background levels. A statistically significant correlation between the organic matter content of the soil and the Cr concentration has not been demonstrated. Rapid accumulation of chromium does not occur; it ranges from 10 to 20 µg.kg^{-1} per year. In groundwater, values > 1 µg.l^{-1} are measured only in exceptional cases.

Influx via the large rivers, currently about 600-700 tonnes per year, has fallen drastically over the past few years, mainly because the quality of the Rhine water has improved. There is also a downward trend in the average chromium levels in sediments.

The presence of chromium in the air is characterized by a large contribution (about 90% at most) from abroad. The Cr(VI) fraction in the Dutch atmosphere is not known; estimates range from 0.01 to 30%. There are indications that the size of the Cr(VI) fraction depends on the meteorological condition (influence of photo-oxidants). The total (net) deposition on the Netherlands is between 13 and 14 tonnes per year.

Outside the workplace, cigarette smoke is the principal source of chromium in indoor air.

The daily dietary intake of chromium in the Netherlands is estimated at 100 μg.

5. EFFECTS

This chapter is a summary of a background report written for this integrated criteria document on the possible effects of exposure of man and the environment to chromium. This background report (Janus and Krajnc, 1989), which also contains a comprehensive summary of the references reviewed, has been added as a separate appendix (Appendix "Effects").

5.1. HUMAN TOXICITY

5.1.1. Biological function / minimum daily requirement

On the basis of experiments with rats, Cr(III) is considered to be an essential trace element for mammals, including man. Cr(III) is present in biological material as a component of an organic compound, the so-called "glucose tolerance factor", so termed because of its effect on the chemobiokinetics and metabolism of glucose. The effect of chromium on glucose metabolism is insulin-dependent. In addition, Cr(III) is involved in the structure and activity of enzymes (for example, trypsin and phosphoglucomutase), in lipid metabolism and possibly in stabilizing the structure of RNA. Chromium-deficient diets have resulted in impaired glucose tolerance in experimental animals; in severe cases chromium deficiency can lead to a diabetes-like syndrome and retardation of growth. In humans (marginal) chromium deficiency has been associated with malnourished children, pregnant women, aged people and insulin-dependent diabetics.

Based on the chromium concentration in urine and the fractional absorption value for chromium in food from the gastrointestinal tract, the minimum daily dietary requirement for adults is estimated to be 2 to 8 μg Cr(III), equivalent to 0.03 to 0.13 μg Cr(III).kg^{-1} body weight per day.

5.1.2. Chemobiokinetics and metabolism

- Absorption

After oral exposure of experimental animals to inorganic chromium salts, both Cr(III) and Cr(VI) compounds, fractional absorption values of < 0.5% to 6% have been reported. In human studies values of up to 10% have been estimated. On the basis of both animal and human studies, an absorption value of 5% is considered to be an average value for both forms of inorganic chromium (although the fractional absorption value from the gastrointestinal tract is higher for Cr(VI) than for Cr(III), the degree of absorption of both chromium forms after oral intake is similar because Cr(VI) is partly reduced to Cr(III) in the stomach). For organic chromium [Cr(III)] in food, an average absorption value of 25% has been accepted. Quantitative data on the absorption of chromium after inhalation are not available. In view of the particle size distribution of chromium in aerosols in ambient air (the mass median diameter of the majority of chromium particles in ambient air is approximately 1 μg, see chapter 3), a considerable part of chromium in air is deposited in the tracheobronchial and pulmonary regions of the respiratory tract. A study with rats found that chromium is absorbed rapidly after inhalation of respirable zinc chromate dust.

- Transport, distribution, metabolism

Once absorbed, the fate of chromium is dependent on the valence state. Cr(VI) readily passes through membranes, which are considered to be relatively impermeable to Cr(III). Because of this difference, chromium is found in both erythrocytes and plasma of the blood after absorption of Cr(VI) from the gastrointestinal tract, while chromium is found exclusively in the plasma after gastrointestinal absorption of Cr(III). After passing the cell membrane, Cr(VI) is reduced rapidly to Cr(III), which subsequently binds to macromolecules.

After oral or parenteral administration, chromium accumulates especially in liver, kidneys, spleen and bone marrow; some data also indicate a significant accumulation in testicles, brain, heart and lungs. The absolute amount found in the tissues is dependent on both the valence state and the counterion. After exposure by inhalation, the final distribution also depends on the chromium speciation; the major organs in which accumulation occurs are the lungs, kidneys, spleen and liver. Inhalation experiments with rats showed that Cr(VI) may be taken up by the lungs and transported to the red blood cells in which it is reduced to Cr(III). The Cr concentration in human tissues is dependent on age. Levels start to decline soon after birth in some organs and after about 10 years in other organs. The Cr concentration in lungs falls until the age of about 20 years, after which there is a steady increase throughout the remaining part of life.

Water-soluble Cr compounds can be converted in the lungs to insoluble compounds with long residence times.

- Excretion

After oral exposure to inorganic chromium compounds, especially Cr(III) compounds, chromium is recovered mainly in the faeces owing to the low fractional absorption values. Animal studies, in which chromium was administered parenterally, showed that most of the chromium absorbed from the gastrointestinal tract was excreted via the urine.

5.1.3. Toxicity

In this section, specific occupational toxicological data are in principle not considered, unless these data can be used for establishing toxicological recommended values for the general population.

- Short-term exposure

Animals

Acute oral LD50 values for rats range from 20 to 250 mg $Cr(VI).kg^{-1}$ body weight and from 180 to 620 mg $Cr(III).kg^{-1}$ body weight, based on tests with inorganic compounds. On the basis of these LD50 values and experiments in which inorganic Cr compounds were administered parenterally, it is concluded that Cr(VI) is usually more toxic than Cr(III). The only two available subacute/semichronic oral studies are very limited with respect to the number of animals used, the parameters studies and/or the data reported.

In a subchronic study, exposure of mice by inhalation to 30 $mg.m^{-3}$ $CaCrO_4$ "dust" (10 mg $Cr(VI).m^{-3}$) for 5 hours per day on 5 days per week resulted in increased mortality.

Humans

In humans ingestion of 1-5 g "chromate" (not further specified) results in severe toxic effects. The signs and symptoms include gastrointestinal disorders, haemorrhages, hepatotoxic and nephrotoxic effects, and convulsions; such acute poisoning cases may be fatal.

Ulcerations and perforations of the nasal septum were found in workers exposed to "chromate" aerosols at levels ranging from 100 to 300 μg

$Cr(VI).m^{-3}$. Asthmatic attacks, an allergic reaction due to sensitization to Cr(VI), have also frequently been reported.

- Effects on reproduction and teratogenicity

The available data from one oral and one inhalation animal study are too limited to permit an evaluation of possible developmental effects after exposure by these routes.

After parenteral administration of either Cr(VI) or Cr(III) to pregnant hamsters and mice in specific teratogenicity studies, developmental effects were observed, such as increased foetal mortality, growth retardation and internal and external malformations. These effects appear to be associated with maternal toxicity, but the available data are insufficient to permit definitive conclusions on this to be made.

- Long-term exposure

Animals - oral exposure

Most long-term oral studies are considered to be inadequate for a sound evaluation of the toxicity of chromium, because of the parameters studied, the doses used, the numbers of animals used and/or the data reported.

In two studies with Cr(III), rats were fed a diet containing up to 5% insoluble Cr(III) oxide pigment (Cr_2O_3) for 90 days and life, respectively. On the basis of these two studies, the highest dose, equivalent to 1210 mg $Cr(III).kg^{-1}$ body weight per day, is considered to be the no-effect dose. Other long-term studies in which animals were fed diets containing chromium are not available.

In a 1-year study in which rats received the relatively soluble Cr(III) chloride ($CrCl_3$) in their drinking water (25 mg $Cr(III).l^{-1}$), no adverse effects were found. This dose, corresponding to 2.5 mg $Cr(III).kg^{-1}$ body weight per day, is therefore considered to be the no-effect dose. Other studies, in which animals received only one low dose of Cr(III) in the drinking water (corresponding to 0.3-0.5 mg $Cr(III).kg^{-1}$ body weight per day) are considered to be inadequate for establishing a no-effect dose with respect to toxicity.

The only carcinogenicity study available, in which rats were exposed to chromic(III) oxide for life, found no indications that Cr(III) is carcinogenic. The other oral studies are considered to be inadequate with respect to carcinogenicty.

Long-term feeding studies with Cr(VI) compounds are not available.
In a study in which rats were exposed to potassium chromate in their drinking water for one year, the dose used (25 mg Cr(VI).l^{-1}, equivalent to 2.5 mg Cr(VI).kg^{-1} body weight per day) caused no adverse effects. Other studies in which animals were exposed to Cr(VI) in drinking water are considered inadequate to establish a no-effect dose with respect to toxicity.
In a 3-generation study in which mice received potassium chromate in their drinking water (500 mg K_2CrO_4.l^{-1}, equivalent to 9 mg Cr(VI).kg^{-1} body-weight per day), no indications of carcinogenic activity were found. The other studies with Cr(VI) are considered to be inadequate for conclusions on carcinogenicity to be drawn.

Animals - exposure by inhalation and parenteral administration
The carcinogenicity of chromium, especially with regard to lung tumours, has been studied in a number of inhalation tests and in studies using implantation or injection techniques. Although no lung tumours were observed in inhalation studies using different animal species and chromium compounds, local malignant tumours in lungs and other tissues of experimental animals have been induced after implantation and injection techniques, especially in rats. The evaluation of the International Agency for Research on Cancer (IARC, 1980) concluded, on the basis of all animal studies, that there is sufficient evidence for the carcinogenicity of calcium chromate (which is a water-soluble compound) and a number of relatively insoluble Cr(VI) compounds (sintered calcium chromate, lead chromate, strontium chromate, zinc chromate and sintered chromium trioxide) in rats. Furthermore, the IARC (1980) concluded that there is limited evidence for the carcinogenicity of lead chromate(VI) oxide and cobalt-chromium alloy in rats. The data were considered inadequate for the evaluation of the carcinogenicity of the other Cr(III) and Cr(VI) compounds tested.

Epidemiological data
In epidemiological studies an association has been found between occupational exposure to chromium compounds and mortality from lung cancer, especially in the chromate-producing industry. An increased frequency of chromosomal aberrations has been observed in workers exposed to chromium(VI) compounds. On the basis of these studies, the IARC (1980)

concluded that there is sufficient evidence of respiratory carcinogenicity in humans occupationally exposed during chromate production. Data on lung cancer risk in other industries in which workers are exposed to chromium products, and on cancer at sites other than the lungs are considered to be insufficient. According to the IARC (1980), the available epidemiological evidence does not permit a distinction between the relative carcinogenicity of chromium compounds of different oxidation states or solubilities, but it appears that exposure to a mixture of Cr(VI) compounds of different solubilities (as found in the chromate production industry) carries the greatest risk to humans.

A number of epidemiological studies, which also include data on exposure levels, have been described and evaluated by two different scientific committees, one from the World Health Organization (WHO, 1987) and one from the U.S. Environmental Protection Agency (U.S. EPA, 1984). On the basis of these studies these committees have calculated the carcinogenic potency of hexavalent chromium. The calculations were based on measured or estimated Cr(VI) levels in the air, because this valence state is considered to be carcinogenic (see also the section "Genotoxicity"). On the basis of the available adequate studies, the carcinogenic potency of Cr(VI) has been expressed as the "unit risk" (UR), defined as the extra lung cancer risk occurring in a hypothetical population in which all individuals are exposed continuously throughout their whole lives to a concentration of 1 μg $Cr(VI).m^{-3}$ in the air they breathe.

On the basis of three different studies, the WHO (1987) considered a "Unit Risk" of 40×10^{-3}, the geometric mean of the risk estimates of these three studies, to be the best possible estimate of the carcinogenic potency of Cr(VI). The U.S. EPA (1984) considered the study by Manusco et al. (1975) the most suitable for an estimation of the cancer risk, resulting in a "unit risk" of 12×10^{-3}.

- Genotoxicity

Cr(VI) compounds cause mutations and allied effects in a wide range of prokaryotic and eukaryotic systems, both *in vitro* and *in vivo*, whereas Cr(III) compounds are not active in similar test systems, or only at extremely high, cytotoxic concentrations. Therefore it is concluded that Cr(VI) is mutagenic and Cr(III) not mutagenic. The mutagenicity of Cr(VI) is decreased or abolished by reducing agents such as human gastric juice and the microsomal fraction from rat liver. The difference between the mutagenic activity of Cr(VI) and Cr(III) can be explained by differences in physicochemical properties. For example, Cr(VI) readily penetrates cellular membranes whereas Cr(III) does not.

5.2. ECOTOXICITY

5.2.1. Aquatic organisms

- Accumulation

The highest chromium concentrations, up to 1000-3000 mg.kg^{-1} dry weight, have been found in experimental studies with unicellular algae. For example, in two long-term experiments, freshwater populations exposed to 50 μg Cr(VI).l^{-1} had concentrations of 500 and 1450 mg.kg^{-1}; the resulting bioconcentration factors (BCF= $C_{organism}$: C_{water}) were 10,000 and 29,000, respectively. In algae collected at three locations in the River Rhine chromium levels were much lower: 0.50, 0.7 and 26 mg.kg^{-1} dry weight at concentrations in the water of 1.8, 35 and 120 μg Cr.l^{-1}, respectively (the resulting BCFs were 270, 20 and 215, respectively). The accumulation of chromium in freshwater algae is predominantly a physicochemical (adsorption) process.

The concentrations measured in invertebrates collected from polluted waters are in general not much higher than those measured in invertebrates from unpolluted waters: $\leq$ 25 mg.kg^{-1} dry weight versus $\leq$ 5 mg.kg^{-1} dry weight. The average concentrations on the basis of wet weight are usually $\leq$ 10 mg.kg^{-1}. In accumulation studies with invertebrates (molluscs and worms), BCFs ranging from 125 to 200 have been measured for exposure to both Cr(III) and Cr(VI). In a laboratory study, exposure of two species of marine molluscs (including the common edible *Mytilus edulis*) to as much as 1000 μg Cr(III).l^{-1} in natural sea water resulted in much higher concentrations: 430 and 765 mg.kg^{-1} dry weight, respectively.

Concentrations in different species of fish ($\leq$ 5 mg.kg^{-1} wet weight) are much lower than those in invertebrates. Chromium levels in omnivorous and carnivorous species of fish were found to be similar, indicating that there is no relationship with feeding habits. The concentrations given for invertebrates and vertebrates (fish) apply to both freshwater and seawater organisms.

It can be concluded that chromium is accumulated to a limited extent by aquatic invertebrates and vertebrates. In view of the decreasing concentration in organisms with increasing trophic level ($C_{algae} > C_{invertebrates} > C_{vertebrates}$), it is also concluded that biomagnification (accumulation through food chains) of chromium is insignificant.

- Toxicity

Since the vast amount of literature data on chromium includes many data on toxicity after long-term exposure, this section has focused especially on this aspect.

Unless otherwise stated, the concentrations reported herein are "total" chromium concentrations ("dissolved" [particle size < 0.45 μm] plus "undissolved"), expressed in $\mu g\ Cr.l^{-1}$.

Toxicity to freshwater organisms

Short-term (24-96 hours) "single species" tests with most species of invertebrates have resulted in EC50 and LC50 values of 2,000 to 60,000 $\mu g.l^{-1}$, based on tests with both Cr(III) and Cr(VI). Crustaceans, especially cladocerans (*Daphnia sp.*) are the most sensitive invertebrates, with many acute L(E)C50 values in the 10 to 500 $\mu g.l^{-1}$ range. Most of these values are based on tests with Cr(VI). In general, fish are slightly less sensitive than invertebrates: acute LC50's range from 3,000 to 190,000 $\mu g.l^{-1}$, based on tests with both Cr(III) and Cr(VI). Abiotic factors which may have a major influence on the toxicity of Cr(VI) are the hardness and pH of the water: the lowest L(E)C50 values have been found at low hardness (ca 50 $mg.l^{-1}$ as $CaCO_3$) and low pH (<7).

Long-term single "species tests" (n = 35 species) with Cr(VI) have resulted in NOEC values of 0.35 to 6,650 $\mu g\ Cr(VI).l^{-1}$. The extremely low value of 0.35 $\mu g\ Cr(VI).l^{-1}$ was found in a test with the diatom *Stephanodiscus hantzschii* in very soft water (hardness 8 $mg.l^{-1}$ as $CaCO_3$), a species which is common in hard, eutrophic waters. Relatively low values (10 to 100 $\mu g\ Cr(VI).l^{-1}$) have been reported for representatives of important taxonomic groups, namely algae, crustaceans and fish. In general, fish are less sensitive than algae and invertebrates. The few NOEC values from long-term tests (n = 4 species) with Cr(III) range from 48 to 330 $\mu g\ Cr(III).l^{-1}$ (NOECs from secondary literature sources have been disregarded because the reliability and test conditions could not be ascertained).

In experimental micro-ecosystems (algae) a concentration of 100 $\mu g\ Cr(VI).l^{-1}$ has resulted in changes in the community composition.

Toxicity to marine organisms

Short-term "single species" tests with 18 different species of both invertebrates and vertebrates have resulted in L(E)C50 values of 2,000 to 105,000 μg Cr(VI).l^{-1}. The lowest values (≤ 7,500 μg Cr(VI).l^{-1}) have been reported for crustaceans and polychaete worms. The few L(E)C50 values for Cr(III), 10,000 to 56,000 μg Cr(III).l^{-1} (n = 3 species) lie in the same range as those for Cr(VI).

Long-term "single species" tests (n = 5 species) with Cr(VI) have resulted in NOECs of 13 to 770 μg Cr(VI).l^{-1}, the lowest value being found for a species of worm. The only available NOEC resulting from a test with Cr(III) is 50,400 μg.l^{-1} "total" Cr(III); in this test only 20 μg.l^{-1} was found to be "dissolved" Cr(III) (< 0.1 μm). Based on this NOEC value and two NOLC values (≥ 10,000 μg Cr(III).l^{-1}), it is concluded that Cr(III) is less toxic than Cr(VI) in sea water, which is explained by the poor solubility of Cr(III) in sea water.

In an experimental micro-ecosystem consisting of algae, an inverse relationship was found between toxicity and salinity. At "low" salinities (0.03 o/oo and over), a concentration of 100 μg Cr(VI).l^{-1} either completely eliminated growth or greatly reduced the rate of growth, whereas at "medium" to "high" salinities (up to 32 o/oo) growth was not affected.

- Accumulation and toxicity in water-sediment systems

The bioavailability of trace metals, including chromium, to aquatic organisms is dependent on hydrodynamical, geochemical and biological mechanisms. Few specific data on chromium are available. In an aquarium experiment in which two species of marine bivalve molluscs were exposed to suspensions of natural sediments in sea water, the filtration rate was reduced at concentrations ≥ 150 mg Cr(III).kg^{-1} clay; exposure to 10 mg Cr(III).kg^{-1} clay had no effect. The clay content of these sediments was not specified.

5.2.2. Terrestrial organisms

Most data in this section refer to Cr(III), by far the most stable form of chromium in soils (see chapter 3).

- Accumulation

All data available on accumulation in terrestrial organisms concern earthworms.

In a test carried out for this integrated criteria document in which earthworms of the species *Eisenia andrei* were exposed in an artificial soil (8% clay, 8% organic carbon [OC], pH 6.0) to Cr(III) concentrations of up to 1000 $mg.kg^{-1}$ dry weight (added as a solution of Cr(III) nitrate) for three weeks, a dose-related increase in the chromium concentration in the worms was found. Bioconcentration factors ($BCF = C_{organism} : C_{soil}$, on a dry weight basis) were 0.03-0.05 at the lowest concentrations and 0.02 at the highest concentrations tested. After transfer of the worms to untreated soil a rapid elimination of chromium occurred; after 3 weeks, only the level in worms exposed to the highest concentration was still slightly increased compared to the controls (1.1 versus 0.7 $mg.kg^{-1}$ dry weight).

Earthworms, collected from a pasture on an untreated soil with chromium levels in the top layer of 13 to 21 $mg.kg^{-1}$ dry weight, contained 3-7 (average 4) $mg.kg^{-1}$ dry weight. After treatment of the pasture with different amounts of contaminated sludge for several years (resulting in soil Cr levels in the top layer of 25 to 400 $mg.kg^{-1}$ dry weight), the worms contained 7-17 (average 11) $mg.kg^{-1}$ dry weight. However, the levels in the worms were independent of the amount of sludge applied. In another field study conducted in the Netherlands, maximum concentrations of 8 to 10 $mg.kg^{-1}$ dry weight were found in worms collected from 6 different agricultural soils treated with compost; maximum concentrations in the soil were 110-125 $mg.kg^{-1}$ dry weight. Similar results have been obtained in other studies. The highest reported level in worms is about 50 $mg.kg^{-1}$ dry weight, and was found in a study in which worms were collected from a wide range of soils.

On the basis of these data it is concluded that the Cr level in earthworms does increase with increasing chromium concentrations in the soil, but the extent of accumulation is also determined by other soil parameters. Worms always have much lower chromium levels, often by a factor of 10, than soil samples, indicating that chromium is not concentrated from the soil by these organisms.

- Toxicity

Most data on toxicity refer to microbes (numbers, diversity) and microbe-mediated processes (respiration, ammonification, nitrification, enzyme activities). The other data concern invertebrates (earthworms).

Microbes and microbe-mediated processes

In some short-term studies (exposure times ranging from a few hours to several weeks), (reversible) effects on respiration, mineralization, and/or ammonification were found at concentrations of 25 to 100 $mg.kg^{-1}$ dry weight (expressed as Cr(III) or "chromium"). However, in most studies no effects were observed at concentrations up to 150-200 $mg.kg^{-1}$ (dry weight). At concentrations of 150 to 350 $mg.kg^{-1}$ (dry weight) data are not consistent: in some studies inhibition of these processes was found, while in other studies no inhibition or even stimulation was noted. These microbe-mediated processes were inhibited in most cases at concentrations $\geq$ 400 $mg.kg^{-1}$ (dry weight).

In the few long-term studies available (exposure times varying from a few months to approximately one year) concentrations up to 200 $mg.kg^{-1}$ (dry weight) [Cr(III), "chromium"] usually did not cause irreversible effects. In a laboratory study with 5 different, representative Dutch soils (including 2 sandy soils) a statistically significant inhibition of the parameters studied (respiration, activity of several enzymes, numbers of microorganisms) was found only occasionally at concentrations up to 400 mg $Cr(III).kg^{-1}$ dry weight. The EC50 value with regard to the activity of the enzyme arylsulphatase was in 2 of the soils studied less than 400 (10 and 180, respectively) mg $Cr(III).kg^{-1}$ dry weight. EC50 values for the other enzymes tested were $\geq$ 400 mg $Cr(III).kg^{-1}$ dry weight. Cr(III) was added to the soils as $CrCl_3$.

Cr(VI) is much more toxic than Cr(III): the lowest effect-concentrations are 1 to 10 mg $Cr(VI).kg^{-1}$.

Invertebrates

In a test carried out for this integrated criteria document with the earthworm *Eisenia andrei* in an artificial soil (8% clay, 8% OC, pH 6.0), only the highest concentration tested (1000 mg $Cr(III).kg^{-1}$ dry weight) resulted in adverse effects on growth and reproduction; the NOEC is 300 mg $Cr(III).kg^{-1}$ dry weight (based on measured concentrations). In this test the worms were exposed for 3 weeks to treated soil (Cr(III) was added to the artificial soil as chromium(III) nitrate, in solution), followed by a 3-week recovery period in untreated soil. The only other test in which earthworms were exposed to Cr(III) is considered to be outside the scope of this document because of the method used (soil covered with chromium-treated sludge).

Cr(VI) appears to be much more toxic than Cr(III): two tests with species of earthworms not found in the Netherlands resulted in increased mortality after 8 weeks of exposure to the lowest concentrations tested, 2 and 10 mg $Cr(VI).kg^{-1}$, respectively. In both tests the worms were transferred once a week to fresh soil treated with a potassium dichromate solution.

5.3. TOXICITY TO AGRICULTURAL CROPS AND LIVESTOCK

5.3.1. Agricultural crops

In a number of studies additions to the soil of Cr(III), but not Cr(VI), have produced effects such as increased yields of crops. However, there is no conclusive evidence that Cr(III) is essential to plants.

Most data in this section refer to Cr(III), by far the most stable form of chromium in soils.

- Accumulation

Chromium is usually present in plants. For example, vegetables from 25 plant families were found to contain from 0.01 to 1.0 mg $Cr.kg^{-1}$ dry weight. Chromium is accumulated mainly in the roots: the level in roots is approximately a factor of 5 to 250 higher than in shoots. The root-shoot ratio increases with increasing soil chromium concentration. Levels in the above-ground parts of crops grown on uncontaminated soil usually do not exceed 0.5 $mg.kg^{-1}$ dry weight . These relatively low levels are consistent with the low chromium concentrations in soil solutions, also after extraction with, for example, a 1 M KNO_3 solution, indicating a low bioavailability of chromium in soil. Levels in shoots of $\geq$ 3 $mg.kg^{-1}$ dry weight probably indicate an increased accumulation, but in view of the low concentrations in control plants, contamination with soil may obscure actual uptake.

In a pot experiment, additions to the soil of 350 and 700 $mgCr(III).kg^{-1}$ dry weight (added as chromic acetate) resulted in shoot chromium concentrations of 15-46, 26-58 and 4-7 $mg.kg^{-1}$ dry weight in the first (maize), second (rye) and third (maize) crop, respectively. The control levels in the crops were < 3 mg.kg^{-1} dry weight. In soil amended with treated sludge - resulting in similar chromium concentrations in the substrate - shoot chromium levels were significantly lower: 5-8, 5-10 and ≤ 3 mg.kg^{-1} dry weight in the first, second and third crop, respectively. Additional data from both pot experiments and field tests show that the chromium content of above-ground parts of food crops is not, or only a little, affected when plants are grown in soils treated with chromium-containing sludge, resulting in substrate concentrations of up to about 400 mg.kg^{-1}. In a pot experiment conducted in the Netherlands the accumulation in oats of Cr(III) from different soils, with an added concentration of 800 mg Cr(III).kg^{-1} dry weight, was studied. Concentrations in the immature crop were ≤ 150 mg.kg^{-1} dry weight (clay soils, sandy soil with 19% OC) and 500-800 mg.kg^{-1} dry weight (sandy soils with 3-7% OC). In barley, grown on a sandy soil with additions of 200 mg Cr(III).kg^{-1} or 200 mg Cr(VI).kg^{-1}, concentrations in the above-ground parts (2-3 mg.kg^{-1}) were only slightly increased compared with the controls (0.5-0.8 mg.kg^{-1}).

In a pot experiment in which four food crops were grown on five different fluvial soils (reclaimed or dredged sediments) with chromium concentrations ranging from 100 to 600 mg.kg^{-1} dry weight, the crops contained similar levels, < 1.5 mg.kg^{-1} dry weight, irrespective of the soil chromium concentration. Only the concentrations in radish tubers increased with increasing soil chromium levels, but the highest concentration was only four times higher than the lowest concentration. The concentrations in potato tubers grown on substrates with high chromium levels (harbour sludge, soils treated with compost) were not increased: all concentrations were in the range from 0.2 to 0.4 mg.kg^{-1} dry weight, corresponding to 0.05-0.1 mg.kg^{-1} fresh weight.

It can be concluded that chromium is accumulated to a relatively small extent in the above-ground parts of crops. After addition to soils of inorganic chromium, concentrations in crops are higher than after addition of chromium in the form of sludge or compost.

- Toxicity

In a pot experiment with 6 representative Dutch soils - 3 loamy clay soils and 3 sandy soils - additions of up to 200 mg Cr(III).kg^{-1} dry weight did not reduce the yield of oats. The same results have been obtained in other

experiments. In both pot and field experiments in which crops were grown on substrates with high chromium levels (fluvial clay soils, soils treated with sludge), chromium concentrations of 350 to 500 mg.kg^{-1} (total Cr) in the substrate did not result in yield reduction. When these concentrations are reached after one single application, reductions in yield may occur in the first crop(s).
Cr(VI) is much more toxic than Cr(III): in studies with different soils and crops the lowest effect-concentrations ranged from 10 to 80 mg Cr(VI).kg^{-1}.

5.3.2. Livestock

Data on livestock are very limited. On the basis of data on experimental animals (see 5.1.) it is assumed that Cr(III) is also essential to farm animals, but specific data on this are not available.

Accumulation

Quantitative data on the absorption of chromium from the gastrointestinal tract are not available. On the basis of data presented in 5.1., a mean absorption value of 25% is estimated for chromium in fodder.
Chromium levels of 30 mg.kg^{-1} in liver and 4 mg.l^{-1} in blood are considered to be indicative of excessive exposure.

- Toxicity

A single oral dose of 30-40 and 700 mg Cr(VI).kg^{-1} body weight has been reported as the acute lethal dose for young calves and mature cattle, respectively.
No adverse effects were observed in cattle and sheep exposed to 2000 mg Cr(III).kg^{-1} feed, and in chickens fed 330 mg Cr(III).kg^{-1} feed. Cattle and sheep were exposed for periods of several weeks; the exposure time for chickens was not specified.
Cr(VI) compounds have been fed to chickens at levels of about 30 mg Cr(VI).kg^{-1} feed without adverse effects; the exposure time was not stated.
An EEC document on sewage sludge application to agricultural soils concluded that it is very unlikely that applications of chromium-containing sludge to grasslands result in toxic effects in grazing animals.

5.4. SUMMARY AND TOXICOLOGICAL RECOMMENDED LEVELS

5.4.1. Humans

Cr(III) is an essential trace element for mammals. It is estimated that the minimum requirement for adults is provided by a daily dietary intake of 2 to 8 μg Cr(III), corresponding to 0.03 to 0.13.kg^{-1} body weight per day.
Cr(VI) is considered to be a genotoxic carcinogen in mammals, including man. Therefore a threshold value below which Cr(VI) is not carcinogenic cannot be established.
Parenteral administration of either Cr(III) or Cr(VI) to pregnant hamsters and mice in specific teratogenicity studies resulted in increased mortality and malformations in the offspring, among other effects. Developmental toxicity tests in which animals were exposed orally or by inhalation are very limited and definite conclusions about the risk to man cannot therefore be drawn.

- Oral exposure

The available oral studies on Cr(III) are considered to be too limited to establish a maximum acceptable daily intake. Based on feeding studies with insoluble chromic(III) oxide pigment (Cr_2O_3), a no-effect dose of 1210 mg Cr(III).kg^{-1} body weight per day was established; assuming an (estimated) fractional absorption value of 0.5%, this is equivalent to 6 mg absorbed Cr(III).kg^{-1} body weight per day. Based on a study in which animals received relatively soluble chromic(III) chloride ($CrCl_3$) in drinking water, a no-effect dose of 2.5 mg Cr(III).kg^{-1} body weight per day was established; assuming a fractional absorption value of 5%, this corresponds to 0.125 mg absorbed Cr(III).kg^{-1} body weight per day.
Since Cr(VI) is considered to be a genotoxic carcinogen, exposure to Cr(VI) should be as low as possible.

- Exposure by inhalation

Exposure to Cr(III) by inhalation results in a daily intake which is less than 0.1% of the dietary intake (see evaluation, chapter 7). Since there are no indications that inhalation of Cr(III)) causes different effects to oral intake, only exposure to Cr(VI) by inhalation is considered to be relevant.

Although differences have been found in the carcinogenic potency of different Cr(VI) compounds, it is not possible to quantify these differences.
The "unit risk" of 40 x 10^{-3}, calculated by the World Health Organization (WHO, 1987), defined as "the extra lung cancer risk occurring in a hypothetical population in which all individuals are exposed throughout their whole lives to a concentration of 1 μg Cr(VI).m^{-3} of air", is considered to be the best estimate of the carcinogenic potency of Cr(VI). Assuming an acceptable risk of 1 x 10^{-6} (one extra case of lung cancer per million persons exposed lifelong), this risk corresponds to an airborne concentration of 25 x 10^{-6} μg Cr(VI).m^{-3} [0.025 ng Cr(VI).m^{-3}].

5.4.2. Aquatic environment

At present there are no generally accepted methods for extrapolation of the results of laboratory (mostly single species) tests to natural ecosystems. Therefore, different theoretical methods are used provisionally to calculate recommended levels for the aquatic environment from single species tests. The extrapolation methods used in this document are described in detail in a proposal of a committee of the Health Council on the ecotoxicological risk assessment of substances (Gezondheidsraad, 1988). In the present risk assessment the use of these methods is in accordance with the proposal of the Health Council.
In the method according to Slooff et al. (1986), calculated concentrations are based on one toxicity value, either an L(E)C50 from a short-term test or an NOE(L)C from a long-term test. In both cases the value chosen is the lowest value that is reliable and relevant. Using an L(E)C50 two different concentrations can be calculated, namely an NOEC for single species ($NOEC_{ss}$) and an NOEC for ecosystems ($NOEC_{eco}$). Using an NOEC, only an $NOEC_{eco}$ can be calculated. The values calculated must be divided by an "uncertainty factor" which depends on the formula used. The final results are considered to be "safe" concentrations.
In the method according to Kooijman (1987), all relevant L(E)C50 values from long-term tests are used. Using these data, a HCS ("hazardous concentration for sensitive species") is calculated. At this concentration, there is a probability (for example 10%, arbitrarily chosen) that up to 50% of individuals of the most sensitive species will die at long-term

exposure. When there are insufficient long-term L(E)C50 values available, this method can also be applied to L(E)C50 values from short-term tests.
In the method according to van Straalen (1987), which has been derived from Kooijman's method, all relevant long-term NOEC values are used. The calculated HC5 ("hazardous concentration for 5% of the species") is the concentration at which there is a probability of 5% that adverse non-lethal effects will occur in up to 5% of the exposed species in an ecosystem at long-term exposure. The values of 5% are also arbitrarily chosen. The HC5 is considered to be a "toxicological limit value".
Because of the large number of long-term NOEC values available for chromium, only these values have been used in the present risk assessment; extrapolation methods using L(E)C50 values have therefore been disregarded. The results are summarized in table 5.1. By far the most NOEC values are from tests with Cr(VI) in fresh water; the distribution of these values is shown in figure 5.1.

<u>Table 5.1.</u> Calculated concentrations (in $\mu g.l^{-1}$) in fresh water and sea water, based on the methods of extrapolation according to Slooff et al. (1986), Kooijman (1987) and van Straalen (1987)

		Fresh water		*Sea water**
		Cr(VI)	*Cr(III)*	*Cr(VI)*
Lowest relevant NOEC (long-term tests)		*10 ***	*48*	*13*
Number of NOEC values (long-term tests)		*m=35*	*m=4*	*m=5*
Slooff et al.				
$NOEC_{eco}$:UF		*0.9*	*3.4*	*1.1*
Kooijman [1]	*HC*	*0.005*	*0.3*	*0.0004*
Van Straalen [2]	*HC*	*7.0*	*11.2*	*1.3*

** A reliable NOEC for Cr(III) in sea water is not available.*
*** This value is based on two NOECs, namely 9 $\mu g.l^{-1}$ for a crustacean (Atlanto-astacus pallipes) and 11 $\mu g.l^{-1}$ for an aquatic plant (Lemna minor).*
m Number of reliable NOECs, for m different species.
UF "Uncertainty factor".
[1] Dm taken from table 1 in Kooijman (1987) at d = 0.1; theoretical number of species in the ecosystem ("n") is 1000.
[2] Dm taken from table 1 in Kooijman (1987) at d = 0.05.

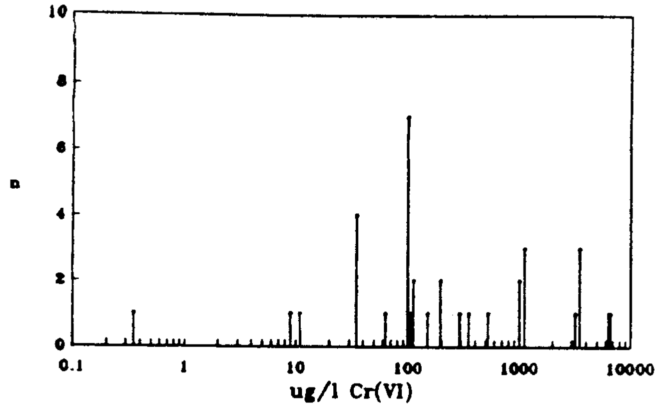


Figure 5.1. Distribution of NOEC values of Cr(VI) in fresh water

All NOEC values used in the methods according to van Straalen (1987) and Kooijman (1987) are printed in bold type in tables 2.1., 2.2. and 2.3. of the Appendix "Effects". In all cases where two or more NOECs are available for one single species, only one value has been used. This value has been selected on the basis of both test procedure (reliability, test medium, exposure duration, effect-parameters) and representative value for the species involved. Therefore, only NOEC values from primary literature sources have been used.

Fresh water

Based on both L(E)C50 and NOEC values it is concluded that there is no relevant difference in toxicity to freshwater organisms between Cr(VI) and Cr(III), the valence states in which chromium occurs. Therefore, one recommended value for chromium in fresh water is proposed. Since there are experimental long-term NOECs available for a large number of species, the recommended value is calculated on the basis of these values using (in the first instance) the method according to van Straalen (1987). By far the most NOEC values (35 of 39) are from tests with Cr(VI), so that the result of this method using these NOECs (7 $\mu g.l^{-1}$) is considered to be the most reliable recommended value for chromium [Cr(VI) plus Cr(III)] in fresh water. This value is based on "total" chromium concentrations ("dissolved" plus "particulate" chromium) in water under laboratory conditions. However,

because of the difference between these conditions and those in surface waters, especially as regards the suspended matter content, the calculated concentration of 7 $\mu g.l^{-1}$ is taken to be "dissolved" chromium (particle size < 0.45 μm).
Assuming a "lowest relevant NOEC" of 10 μg Cr(VI)$.l^{-1}$, an $NOEC_{eco}$ of 30.2 $\mu g.l^{-1}$ is calculated with the method according to Slooff et al. (1986), which, using the uncertainty factor, results in a concentration of 0.9 $\mu g.l^{-1}$.
The difference between the results of the extrapolation methods according to van Straalen (1987) and Slooff et al. (1986) is less than a factor of 10. In accordance with the recommendation of the Health Council, the concentration of 7 $\mu g.l^{-1}$ ["dissolved" chromium, Cr(VI) plus Cr(III)] calculated according to van Straalen is therefore proposed as the toxicological recommended value for fresh surface waters. Based on the data in chapter 4, this concentration corresponds to a "total" chromium concentration of approximately 50 $\mu g.l^{-1}$ in the Dutch surface waters.

<u>Comment</u>: In the calculation according to Slooff et al. (1986), the exceptionally low NOEC (0.35 $\mu g.l^{-1}$) for <u>Stephanodiscus hantzschii</u> has been disregarded, whereas this value has been used in the calculations according to van Straalen (1987) and Kooijman (1987). The reason for this is as follows: the method of Slooff et al. is based on a relationship between the experimental NOEC values for single species and those for ecosystems. In deriving this relationship, data on different, arbitrarily chosen species with different sensitivities have been used. Since only one value per species is used in this method, the use of an exceptionally low value (which is known on the basis of the other available data to be exceptionally low !) will obviously result in an extremely low "safe" value (in this case: 0.05 $\mu g.l^{-1}$). In the method according to van Straalen as well as Kooijman, all available NOEC values are used and the result is partly also determined by the scatter in these NOECs, so that all values must be used in these methods.

<u>Sea water</u>

The concentration calculated according to the method of van Straalen (1987) - on the basis of tests with Cr(VI) - is 1.3 $\mu g.l^{-1}$. This value is based on only 5 NOECs from tests with representatives of only two taxonomic groups (worms and crustaceans). The lowest relevant NOEC for these organisms is the same as that for freshwater organisms. Therefore, and also because of the low solubility of Cr(III) in sea water, the same toxicological recommended value for chromium in sea water is proposed as for fresh water: 7 $\mu g.l^{-1}$ "dissolved" chromium [Cr(VI) plus Cr(III)].

5.4.3. Terrestrial environment

There are indications that Cr(III) is also essential to terrestrial organisms such as plants and farm animals, but conclusive evidence is not available. On the basis of the data available, a minimally required, or desirable concentration in soils cannot be established.
In view of the behaviour and occurrence of chromium in soil (chapter 3), it is assumed that chromium is usually present as Cr(III) in this environmental compartment and in substrates such as sludge. Therefore, only data on Cr(III) in soils and applications to soils as chromium-containing sludge are considered relevant.

Most toxicity tests concern microbe-mediated processes. The results of these tests are heavily dependent on test design and soil characteristics, so that in many cases the data are not consistent. Although lower effect-concentrations have been reported, especially after short-term exposure, concentrations up to 200 $mg.kg^{-1}$ (dry weight, expressed as Cr(III) or unspecified "chromium") usually do not cause irreversible effects on microbe-mediated processes after long-term exposure.
In a test with the earthworm *Eisenia Andrei*, carried out for this integrated criteria document, the resulting NOEC (with regard to growth and reproduction) was 300 $mg\ Cr(III).kg^{-1}$ dry weight. Relevant data on other terrestrial organisms are not available.
Accumulation of chromium in the above-ground parts of crops is only slightly increased, if at all, when plants are grown in soils treated with chromium-containing sludge, resulting in substrate concentrations of up to about 400 $mg.kg^{-1}$ dry weight. In soils treated with (soluble) inorganic compounds, additions of up to 200 $mg\ Cr(III).kg^{-1}$ dry weight do not result in yield reduction of crops. Crop yields are usually not reduced when plants are grown on substrates with high chromium concentrations (350-500 $mg\ Cr.kg^{-1}$ dry weight); however, when these concentrations are reached after one single application, reductions in yield may occur in the first crop(s).
Based on the data concerning (a) effects on microbes and microbe-mediated processes such as respiration, ammonification, nitrification and enzyme activities, b) accumulation in, and toxicity to earthworms, and c) accumulation in, and toxicity to crops, it is concluded that soil chromium concentrations up to 200 $mg.kg^{-1}$ do not result in irreversible effects. A

range of 100 to 200 $mg.kg^{-1}$ is provisionally given as the toxicological recommended value in soils, the ecotoxicological acceptable level also being dependent on the clay content (particle size < 2 μm) of the soil. Although there are uncertainties in some of the data reported (speciation of chromium, concentration expressed on a dry or a wet weight basis), they are considered to refer to "total" chromium concentrations expressed on a dry weight basis.

6. EMISSION-CONTROL MEASURES

Developments already in progress, policy-controlled or otherwise, have ensured that the emissions of chromium into water and air have fallen substantially over a period of 10 years. In the discussion on emission-control measures, the emphasis will be on the principal sources identified in chapter 2. A distinction will be made between autonomous developments and additional measures still to be taken to reduce these emissions. Where possible, an estimate of the costs involved in these measures is given. Finally, the financial consequences of measures (particularly important in the case of additional measures) are briefly discussed. As in chapter 2, the sources to be discussed are divided into industrial uses of chromium-containing primary raw materials and waste streams.

6.1. APPLICATION OF CHROMIUM COMPOUNDS

6.1.1. Metal products industry

- Autonomous

Over a period of about 10 years, the metal products industry has cut its chromium discharges into surface water from about 48 tonnes in 1975 to about 9.9 tonnes in 1985 (IMP Water, 1985-1989) by installing wastewater treatment systems (detoxification/neutralization/dewatering systems and ion exchangers). Ros (1986) has calculated that with the existing purification techniques the Cr discharges into water can be reduced to about 10 kg per year per enterprise. This means a maximum annual input to surface water of 3 tonnes for this sector (ca 300 plants).

Cr(VI) emissions into the air have fallen sharply as a result of minimizing mist formation above the chromium bath by providing it with a cover or the use of F-containing surfactants (VOM, 1984), and through the installation of drip catchers. Application of these techniques leads to reduced exposure of workers to Cr(VI) on the one hand, and to a reduction in atmospheric chromium emissions on the other (last-mentioned technique). Drip catchers have an efficiency of 95 to 98% (tel. business inf.; State of California, 1986). Based on about 140 electroplating establishments which carry out a metal treatment producing chromium emissions into air (VOM, 1988), a

reduction of the total atmospheric emission to a maximum of 250 kg per year must be considered feasible.
However, reductions in chromium emissions into water and air have resulted in the generation of metal hydroxide sludges (1500 tonnes d.w. per year). This sludge must be treated as chemical waste, and almost all of it is (currently) exported as such. Further cuts in chromium emissions (water, air, waste materials) are to be expected because of decreased use of chromium compounds and through a combination of process-integrated and the above-mentioned purification techniques.

The current cost of exporting chemical waste varies between Dfl.50 and Dfl.100 per tonne. It is expected to rise to Dfl.300 per tonne or more. The Enabling Act came into force in October 1986, so that the exportation of chemical waste will become much more difficult, certainly when there is an adequate destination for this chemical waste in the Netherlands (C_2 dump) (VROM, 1988d). As a result, the clean and process-integrated techniques which are currently being used to a limited extent only become infinitely preferable, not only on environment-technical but also on economic grounds.

Process-integrated technologies which make efficient use of chromium are available. In the Netherlands research has been conducted into reducing the chromium concentration in waste water by means of a pellet reactor (VOM, pers. comm.). Techniques aimed at chromium reuse are being successfully employed abroad in hard and decorative chromium plating and in chromic acid anodizing. They involve a cascade system of rinsing baths in conjunction with electrodialysis, ion exchangers, etc. Also, techniques are used to extend the life of the chromic acid bath by removing copper and iron impurities by means of ion exhangers in conjunction with evaporation.
A decline in hard and decorative chromium plating has been noted in the past few years. In the blue-passivation of zinc it is possible to replace Cr(VI) with Cr(III), producing a passivated coating of equal quality. The running costs of such a bath are the same or slightly lower than those of the existing commercial baths (Metaalinstituut TNO, 1980). Passivation without chromium may reduce chromium emissions by several percentage points.

6.1.2. Paint application

Unlike in paint production, significant amounts of chromium are emitted during the application of paint. The principal source of these emissions is the spraying of paint in industry (over 9 tonnes in 1986, of which 0.9 tonne into the air and 8.5 tonnes to the soil). This activity also generates chromium-containing spraying waste (about 4 tonnes in 1986).

- Autonomous

The task set for the year 2000 with respect to spraying waste is to achieve a reduction of 50% compared with the amount produced in 1986 by cutting spray losses (reduction to 4.7 tonnes). To achieve this goal, standardization of painting and spraying techniques is being considered. At present the spraying waste is usually disposed of together with other industrial waste, without giving notification that it is chemical waste. In the future the bulk of this waste will be burned as chemical waste. Since spraying waste is produced at many locations, collection within the Small Chemical Waste framework is being considered (VROM, 1988b).

- Additional measures

Measures to reduce these emissions include the use of other spraying techniques or application techniques, improvement of the technical conditions and schooling and/or instruction of paint sprayers.

6.1.3. Leather industry

In leather manufacture, leather is made from hides involving a number of mechanical and chemical treatments. The chemical tanning process takes place batchwise in tan vats (TNO, 1981). Cattlehides are used as raw material in the Netherlands. Sheepskin is no longer produced in the Netherlands.

- Autonomous

The IMP Water (1985-1989) foresees that as a result of the ongoing pollution-abatement measures and changes in the production process, chromium discharges into surface water will fall to about 1.1 tonnes Cr(III) by 1990. Application of the purification techniques mentioned previously resulted in the production of over 3000 tonnes of sludge in

1986, containing about 25 tonnes of chromium. This sludge, together with part of the leather waste, is transported to "De Spinder", a waste dump near Tilburg. The cost of dumping solid waste and chromium sludge in "De Spinder" is about Df125 per tonne, which is similar to the dumping costs for urban waste (Province of North Brabant, pers. comm.; VROM, 1988c).

- Additional measures

One possible way of cutting the volume of chromium-containing sludge is reuse of the chromium still present in the vat after the tanning process. The chromium is first precipitated with calcium carbonate and then dissolved again in sulphuric acid with the formation of chromium sulphate, which can be returned to the processing bath. Recovery systems for this purpose are available and already operational abroad. On the basis of a cost comparison, chromium recycling (depending on the size of the firm) seems to be economically feasible. However, because of contaminations which may occur when using the recovery technique, there is a fear that the quality of the leather will decline. This is reason for the Dutch leather plants which still do their own chrome tanning not (yet) to introduce this recovery technique. However, experience abroad shows that chromium recycling need not be at the expense of the leather quality (VROM, 1988d).
One possible way of reducing the quantity of chromium-containing leather waste is to carry out operations which produce solid waste, such as splitting and clipping, prior to chrome tanning. The resulting waste is chromium-free, is not chemical waste, and can be more easily reused, processed or disposed of. Several firms in the Netherlands have already implemented this measure. Here, too, considerations with regard to quality control of the leather are the reason that this method is not (yet) being introduced on a larger scale (VROM, 1988d; Haskoning, pers. comm.). Another process-integrated technique, still under development, is the production of so-called wet blue. The chrome tanning procedure used is such that the leather contains less than 0.5% chromium, but can be subjected to operations such as splitting, shaving, etc., and is also not liable to deterioration.
Partial de-chroming of leather waste is also known to be possible, because recent research on a laboratory scale has shown that chromium can be removed from solid waste to such an extent that it is no longer chemical waste. This would, for example, make the processing and disposal of the

resulting low-chromium wastes much easier and more attractive (VROM, 1988d).
The above-mentioned processes are still in the research stage, so that (public) data on the costs involved are not yet available.

- Financial consequences

A summary of emission-control measures and, as far as possible, the costs involved, was given in the foregoing sections. This section will consider the financial consequences of implementation of the measures mentioned. First, an outline is given of the nature and size of the firms responsible for chromium emissions. Next, the functioning of the industrial sector (weak and strong points) is analyzed on the basis of the three key variables: market situation, international competition and staying power ('t Gilde et al., 1986). These variables determine the leeway companies have to meet the extra costs of environmental measures.

Structural outline

The Dutch leather industry is a small industrial sector, traditionally concentrated in Central Brabant. In the seventies the leather industry went through a very difficult period: because of the relatively high labour costs and the wastewater treatment requirements, many enterprises went bankrupt and nearly half of the 2000 employees lost their jobs (EZ, 1980). The situation stabilized after 1979: about 1050 persons were employed in 40 enterprises in 1987. It is a fairly small-scale sector: half the enterprises employ fewer than 10 persons (Bedrijfschap, 1988). The leather industry achieved a turnover of Dfl320 million in 1987 (CBS, 1987).
Of the 40 enterprises, only about four carry out all operations from hide to product, including chrome tanning, themselves. A new specialized contracting firm was set up in 1988, which undertakes to tan hides for other companies (Bohmann, 1988). The other enterprises farm out the tanning operation and continue with the processing of pre-tanned leather.

Market situation

Leather and leather products are eminently suitable for an international division of labour. The raw materials (hides) required can be obtained almost everywhere in the world, and the technology is known and not too capital-intensive. Third World countries are quite capable of competing with the developed countries in the leather market, which is consequently worldwide (EZ, 1980).

The leather industry manufactures different types of leather, which are used by various processing industries. The major outlets are the shoe, furniture, clothing and leatherware industries. Upper leather for the manufacture of shoes, accounting for about 60% of total turnover, is by far the most important product (CBS, 1988). Chrome tanning is used in the manufacture of upper leather and upholstery leather (TNO, 1981).

In addition to specialization in different types of leather, the quality of the product is very important in the leather industry. The Dutch leather industry specializes in high-quality products. By combining small-scale, flexible production, high quality and service to the customers, the industry endeavours to serve market segments which are not so sensitive to price changes (EZ, 1980). The advantages of the small-scale production mentioned above and short transport distances should counterbalance the relatively high labour and environmental costs in the Netherlands (Bedrijfschap, 1988).

In the past 10 years the Dutch leather industry has succeeded in acquiring a fairly stable position in a narrow segment of the international leather market. This makes the sector rather vulnerable, also in view of the many small enterprises.

International competition

The leather industry operates in an international market. Seventy per cent of the sales is exported, mainly to EEC countries (Bedrijfschap, 1988). The volume of leather imports and exports is about the same, although the products involved are different. Pre-tanned leather is imported into the Netherlands from countries such as Indonesia, Argentina and the United States.

Staying power

Few data are available on the profitability of the leather industry. Average profits were negative or zero until about 1982. Since 1983 average operating results have fluctuated around 3-4% of turnover, an acceptable percentage (CBS, 1988), but the range is great (EZ, 1980).

Even less is known about the solvency of the sector (the proportion of ownership capital of total capital). One important fact is that the sector is dominated by family firms. This makes enterprises vulnerable because they have fewer possibilities of financing modernization through bank loans, and because problems concerning the succession of the enterpreneur/owner may arise. In the leather industry, variable costs represent 79% of the cost price, of which 2% for energy use. Labour costs account for 15% and depreciation for 2% of the cost price. The leather industry has invested around Df110 million per year over the past few years (CBS, 1988). The cost makeup suggests a moderately labour-, capital- and energy-intensive sector.

The principal characteristics of the leather industry are summarized in table 6.1.

Table 6.1. Summary of relevant characteristics of the leather industry

Structure (business size)	*Small*
Market situation	*Moderate*
International competition	*Strong*
Staying power	*Fair*

The leather industry is a small-scale sector, which has succeeded in acquiring a limited, but stable position in the international market.

6.1.4. Textile industry

- Additional measures

For the fixation by oxidation of sulphur and vat dyes, chromate can be completely replaced with hydrogen peroxide, perborate or (atmospheric) oxygen. Dyes for which chromate must be used in fixation can be replaced with other dyes (DBW/RIZA, 1988).

Because of the complexicity of the overall wastewater problem at the textile-finishing mills and the fact that the available techniques are not yet entirely practicable, it is not possible at present to give details about possible measures.

6.1.5. Wood-impregnating industry

- Autonomous

Chromium emissions to soil, water and air produced during the impregnating process can be almost entirely prevented (Tebodin, 1985). This measure has already been implemented or is in preparation at most firms. The costs vary between Dfl.10,000 and more than Dfl.100,000 per enterprise, depending on its size and the measures already taken (NEHEM, 1986).

The chromium-containing waste produced during cleaning the tanks amounts to 1.7 tonnes per year. This waste has a very high chromium content and is suitable for reuse.

Chromium can leach from freshly impregnated wood when it is not covered during storage. The following preventive measures can be taken against this: fixation of the chromium during impregnation (for example, by steam-fixation) or complete roofing of the storage yard. In steam-fixation, a greatly accelerated fixation reaction takes place, in which Cr(VI) is converted to Cr(III). This reduces the leaching of chromium by 80-90%. Complete roofing can give a similar reduction of leaching.

Impregnated wood must not be used until it has been fixed. The above-mentioned measures only influence the time required for fixation and will therefore have little effect on the leaching of chromium from wood during its use. Steam-fixation has the advantage that the wood can be used on the same day that it has been impregnated, whereas fixation in air under a roof requires at least four days. Since steam-fixation will moreover be considerably less expensive for most firms, it is expected that the former measure will be preferred (tel. business inf.).

As a result of the emission control measures to be taken, the current number of 35 enterprises is expected to fall sharply (tel. business inf.).

6.1.6. Cooling water

- Autonomous

The trend mentioned in chapter 2, in which Cr(VI) is being replaced with chromium-free alternatives, will result in zero emissions by about 1990.

6.2. CHROMIUM-CONTAINING PRIMARY RAW MATERIALS

6.2.1. Titanium dioxide ore-processing industry

- Autonomous

A new technique is being developed for the processing of titanium dioxide ore, which should lead to a reduction in the discharge of chromium into surface water by 90% as of 1-1-1990. The technique is based on the decomposition of ore with coke and chlorine instead of with sulphuric acid which is currently used. In this process, titanium turns into gaseous titanium tetrachloride ($TiCl_4$). Other metals present in the raw material also turn into their respective metal chlorides. After cooling, the titanium tetrachloride is separated from a diversity of solid residues (including the various metal chlorides) and is then separated from various waste gases by condensation.

The remaining "solid" residues are treated with dilute hydrochloric acid, which causes the metals to go into solution. Next, the dissolved metals are mostly precipitated as metal hydroxides by increasing the pH, and filtered off. The filtrate will be discharged as waste water and still contain about 5 to 6 tonnes of chromium on an annual basis. The metal hydroxides sludge, containing about 90% of the original quantity of heavy metals (ca 54 tonnes of chromium), will have to be treated as chemical waste. The total volume of (solid) waste amounts to about 5000 tonnes per year.

The investment for the new factory totals around 250 million guilders. The project is still on schedule and the factory has begun operating in 1990.

6.2.2. Phosphate ore-processing industry

- Autonomous

The source of the current input of heavy metals to the aquatic environment is the wet-chemical processing of phosphate ore. It can be reduced by not discharging the resulting phosphoric acid gypsum or by using phosphate ore with a lower content of heavy metals. Utilization of other types of ore has already led to a reduction in the total discharge of a number of environmentally harmful substances in 1987 despite the 20% increase in waste gypsum discharge. The amount of chromium discharged is probably the same as it was before the use of the other ore types (tel. business inf.).

Application of a cleaner processing technique could also be a possible way of reducing heavy metal emissions. Research into cutting the cadmium emissions by this "clean phosphoric acid technology" has been going on for years. It is estimated that this technique will not be fully developed until 1993 at the earliest (Slooff et al., 1987). Since the development of the clean phosphoric acid process at present is aimed primarily at reducing cadmium and phosphate emissions, its application may not lead to changes in the chromium emissions from the phosphate ore-processing industry and also not to a reduction in the chromium content of the end-product (tel. business inf.; tel. inf. from T.U. Delft).

In addition to research into a cleaner processing technique, extensive research has also been conducted into the possible useful applications of phosphoric acid gypsum. So far it seems that these possibilities do not exist. Its potential use in road building is hampered by the oversupply of pulverized-coal fly ash which, moreover, is qualitatively more suitable for this purpose. This oversupply will become even larger if the coal scenario is adopted for electricity generation. Therefore, the prospect for reusing phosphoric acid gypsum must be regarded as bleak. Kuijenhoven (1986) has estimated that storing this gypsum costs Df120 per tonne, or about 50 million guilders for the total amount of phosphoric acid gypsum produced annually.

The measures which the industries will have to take in the near future to cut the heavy metal discharge into surface waters have recently been laid down in a covenant between the phosphate ore-processing industry and the government. One of the measures is the use of "more environment-friendly" phosphate ore with a lower content of heavy metals in the production process. Its effect on the emissions of chromium is not known. Clarity on this matter will not be provided until factory tests with the new phosphate ore have been carried out. The sector should also examine and elaborate the possible measures aimed at substantially reducing chromium emissions over a 10-year period beginning in 1985. The measures should be based on the best feasible techniques, taking their costs into account.

6.2.4. Power stations

- Autonomous

The prediction of chromium emissions from electricity generating stations for the years 1990-1995 is based on the current Electricity Plan 1987-1996.

An average growth in energy consumption based on the National Energy Survey (ESC, 1987) has been assumed for the years 2000 and 2010. In addition, three variants have been considered in relation to the use of fuel in the electricity sector in the years 2000 and 2010: a coal, a gas and a nuclear variant (KEMA, 1988a). In the light of a newspaper report by the SEP of 25 August 1988 concerning the next Electricity Plan (1989-1998), it may be assumed that the gas variant is most in keeping with this plan. Besides, the next Electricity Plan implies that some 50,000 tonnes of coal-gasification slag will be produced annually as of 1994. The prognoses are presented in table 6.2. (KEMA, 1988b).

Table 6.2. Production of residues by the central power stations, in tonnes of chromium per year

Year	*Bottom ash*	*Pulverized-coal fly ash*	*Gypsum*	*Stack ash*
1990	*19.2*	*142.4*	*0.4*	*0.2*
1995	*20.8*	*148.8*	*0.5*	*0.2*
2000 C	*35.2*	*256.0*	*0.9*	*0.3*
2000 G	*19.2*	*140.8*	*0.5*	*0.2*
2000 U	*24.0*	*176.0*	*0.6*	*0.2*
2010 C	*46.4*	*336.0*	*1.2*	*0.3*
2010 G	*20.8*	*160.0*	*0.6*	*0.2*
2010 U	*14.4*	*104.0*	*0.4*	*0.1*

C = coal variant; G = gas variant; U = nuclear variant

Given the large diversity of heavy metals, their recovery from pulverized-coal fly ash is generally a difficult and expensive process. A few (hypothetical) methods are chloride metallurgy, treatments with suspensions of specific bacteria and acid leaching (followed by extraction or precipitation) (Ros and Slooff, 1987).

Realistic solutions to the environmental load of heavy metals from pulverized-coal fly ash can be provided by fixation of the metals. The cement industry (raw material in the manufacture of portland clinker and mixing element), concrete industry (filler and fine aggregate), road building (filler and foundations) and clayware industry (building bricks, paving stones and Poriso (porous) bricks) offer possibilities in this respect. Since the domestic market is likely to be saturated, opportunities for broadening the range of these applications will have to be found primarily abroad. One possible use which has been tested abroad is the construction of an artificial reef based on pulverized-coal fly ash to benefit the offshore fishing industry.

6.3. CHROMIUM-CONTAINING WASTES

6.3.1. Sewage sludge

- Autonomous

According to the "Waste Prevention and Reuse" memorandum (VROM, 1988b), about 65% of the sludge will be incinerated, about 25% reused and about 5% dumped in the year 2000. To achieve this objective, the following measures have been proposed:

- encouragement of purification techniques producing less sludge,
- construction of incinerating facilities for sludge, and
- establishment of standards for use/application of sludge.

With regard to the chromium emissions from sludge incinerators, it can be noted that the burning of 0.4 million tonnes of sewage sludge (d.w.) will release an estimated 0.05-0.1 tonne of particle-bound chromium into the atmosphere. This estimate is based on the chromium levels in sewage sludge, the standards for dust emissions and observations made in waste incinerators. Furthermore, it is envisaged that in the year 2000 all the sewage sludge from public treatment plants will be burned and/or dumped.
Regarding the standards for the use of sewage sludge, the reader is referred to the "Draft Decree on Quality of other Organic Fertilizers", recently drawn up as part of the Fertilizers Act. It states that up to 1 January 1991 the sewage sludge (d.w.) applied to soils should contain no more than 500 μg chromium.g^{-1}. In 1986 the chromium concentration in sewage sludge from public treatment plants ranged between 3 and 532 $\mu g.g^{-1}$ with an average of 68 $\mu g.g^{-1}$. In addition, a "Draft Decree on Use of other Organic Fertilizers" has been drawn up by the Ministry of VROM under the Soil Protection Act. It gives test values for soils to which sewage sludge is applied. These test values may lead to a decrease in the use of sewage sludge as fertilizer within a relatively short period of time.
As has been mentioned in chapter 2, about 20 tonnes of chromium are diffusely spread on the soil through the use of sewage sludge in agriculture and in the production of compost and organic soil. This diffuse load can be counteracted by dumping or incinerating the sludge under controlled conditions. The cost of dumping (including transport and

dewatering) varies between Dfl.400 and Dfl.700 (Slooff et al., 1987) and that for incineration between Dfl.350 and Dfl.550 (Haskoning, 1988) per tonne dry weight.
Techniques such as bacteria-mediated leaching and acid extraction are mentioned in Slooff et al. (1987) as possible ways of reducing the amount of chromium in sewage sludge. The technical-economic feasibility of these techniques for the total volume of sludge to be processed is not as yet known.

6.3.2. Urban waste

- Autonomous

The policy of the Ministry VROM (VROM, 1988b) on household waste (about 70% of the urban waste) for the year 2000 provides that half the waste (3.9 million tonnes) be incinerated and the other half recycled. To accomplish this task, the following measures are proposed:

- ban on marketing certain products,
- separate presentation and collection of waste components,
- change in the acceptation policy of waste-treatment works,
- increase in the processing tariffs, and
- incineration of non-recyclable domestic waste.

At present, most waste incinerators in the Netherlands are not permitted to emit more particles than 100 $mg.m^{-3}$. A standard of 50 $mg.m^{-3}$ has been established for new plants and existing ones that have to be radically modified. The West-German standard is 30 $mg.m^{-3}$ (TA-Luft, 1986). It is expected that this standard will also have to be met in the Netherlands in the nineties, which is technically feasible by installing certain flue-gas scrubbing systems. This could reduce particle-bound chromium emissions by about 70% depending on, among other factors, the preference of chromium for certain dimensions of the condensation nuclei. An emission level as low as 10 $mg.m^{-3}$ is nowadays realized in concrete projects.
Based on the 1988 value for the average chromium content of urban waste, the developments outlined imply that particle-bound chromium emissions into the air from the incineration of urban waste will be about 0.3 tonne of chromium per year in 2000. The annual costs will be about Dfl.25 to Dfl.45 per tonne of waste, or 100 to 200 million guilders per year for the total volume of urban waste to be burned.

Because of the policy outlined, the amount of residues from waste incinerators in the year 2000 will grow to over 1250 ktonnes per year. The policy aim is that about 80% of this will be reused. To achieve this, measures are proposed such as the establishment of standards and certification with regard to application in (road) building and quality improvement of the slag (VROM, 1988b). However, reuse of residues from waste incinerators will probably be limited, on the one hand because of the expected market saturation, and on the other because of the poor quality in terms of environmental health (e.g. variable composition) compared with pulverized-coal fly ash, which also finds application in road building.

6.3.3. Dredged materials

- Autonomous

Regarding spoil, the policy of the Ministry of VROM (VROM, 1988d) for the year 2000 has established that about 10% is to be reused, about 15% dumped on large-scale disposal sites, and the remainder dumped into salt water, spread on land and stored in small-scale repositories. The concrete measures proposed for this policy are:

- development/direction for use of separation and cleaning techniques; - encouragement of useful application of raw materials (sand/clay) from spoil after seaparation/cleaning;
- prevention of environmentally persistent substances in spoil;
- international approach to pollution of large rivers.

For the removal or fixation of heavy metals in spoil, a study (Rijnmond, 1985) considered flotation, ion exchange, acid leaching, immobilization techniques, thermal techniques and hydrocyclone systems. It was concluded that nearly all techniques are selective. In principle, they could be used for class IV spoil, because this is the most heavily contaminated (and often specifically with heavy metals. It should be noted that chromium is rarely a discriminating parameter in class IV spoil; because of pollution control in cooling towers and electroplating processes in particular, spoil highly contaminated with chromium is no longer found locally.

For the processing of classes II and IIII spoil, a sequence of various techniques would be required, which will lead to excessively high costs. A possible exception is the hydrocyclone, with which in principle spoil can be separated into a less contaminated flow containing coarse particles and a more contaminated flow containing fine particles. Further research will have to show whether the division into two flows produces a more environment-favourable situation. The amounts of classes II and III spoil could diminish several tens of percent with the hydrocyclone method. A rough estimate of the investment costs, based on such a such an system at Hoogovens, is Dfl.45 per tonne of dry matter, and the running costs are of the order of Dfl.20 per tonne of dry matter (Ros and Slooff, 1987).

6.4. SUMMARY AND CONCLUSIONS

Figures 6.1. to 6.3 inclusive present the current (1986) chromium emissions into the environmental compartments air, water (fresh surface water) and soil (diffuse), and also those expected around the year 2000 after pollution abatement. Discharge into waste is shown in figure 6.4. Figure 6.5. presents the current and future emissions into air, water and soil; the input to waste has not been included, because it can be expected that the total amount will remain the same and because the amount in waste dominates the picture too much. Table 6.3. summarizes the consequences of the measures to be taken (on the basis of the autonomous developments outlined) for the emissions. Feasible additional measures are limited. The leather industry can take various additional measures, aimed at chromium reuse and chromium-containing waste reduction. The leather industry is a small-scale sector with a moderate market situation; international competition is strong; its staying power can be characterized as fairly good. It may be possible for the the textile industry to take measures, aimed at replacing chromate with other dyes.

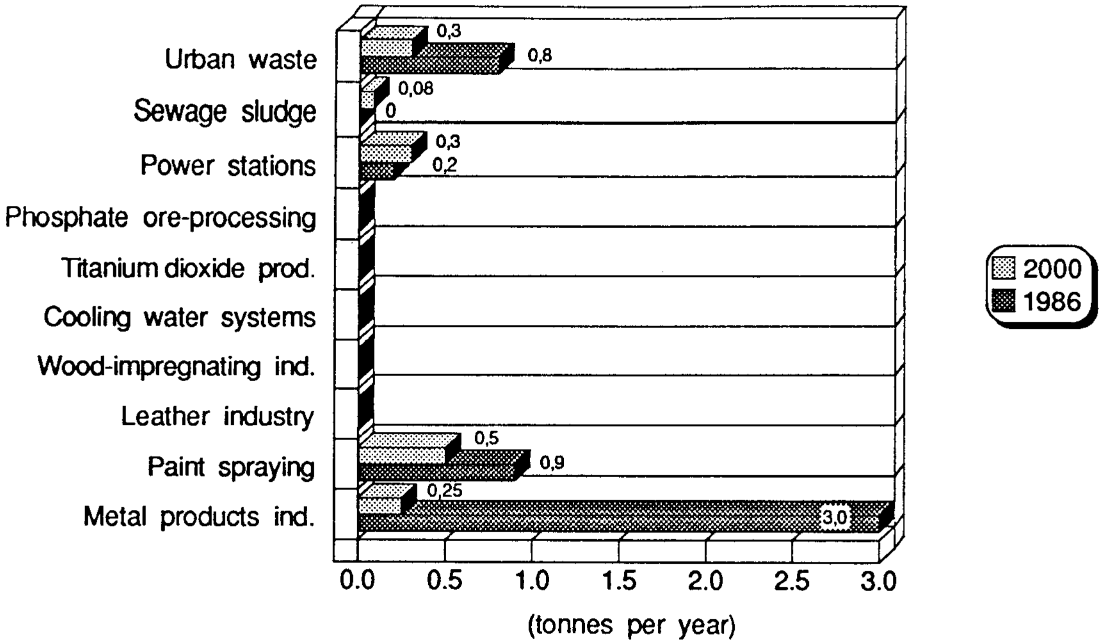


Figure 6.1. *Chromium emissions into air in 1986 and those expected around the year 2000*

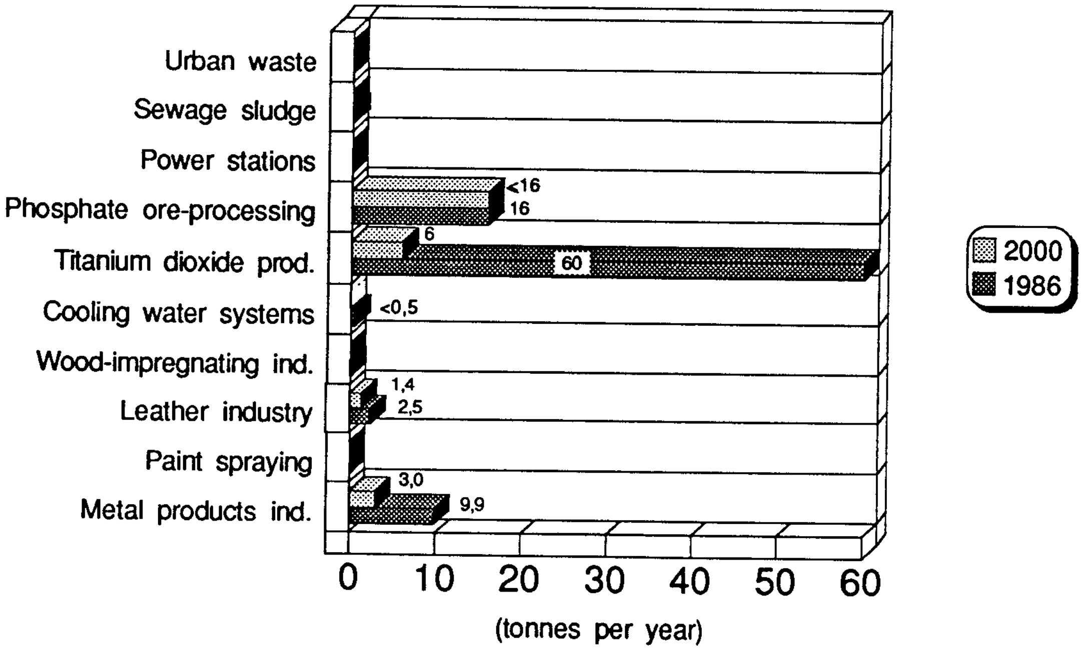


Figure 6.2. *Chromium emissions into (fresh) surface water in 1986 and those expected around the year 2000*

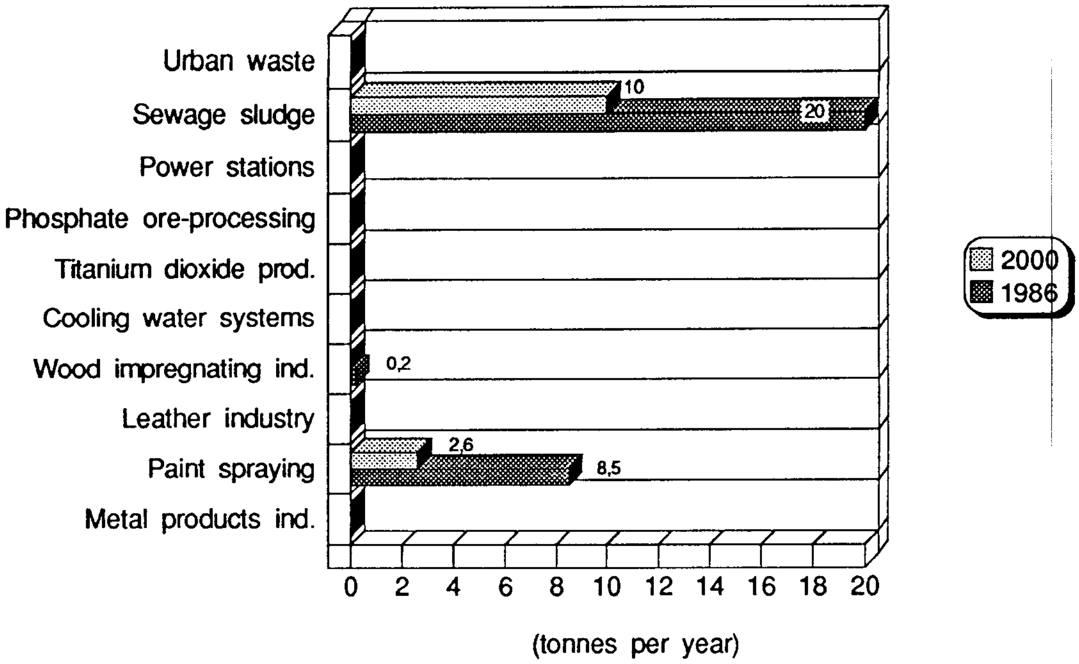


Figure 6.3. *Chromium emissions into soil in 1986 and those expected around the year 2000*

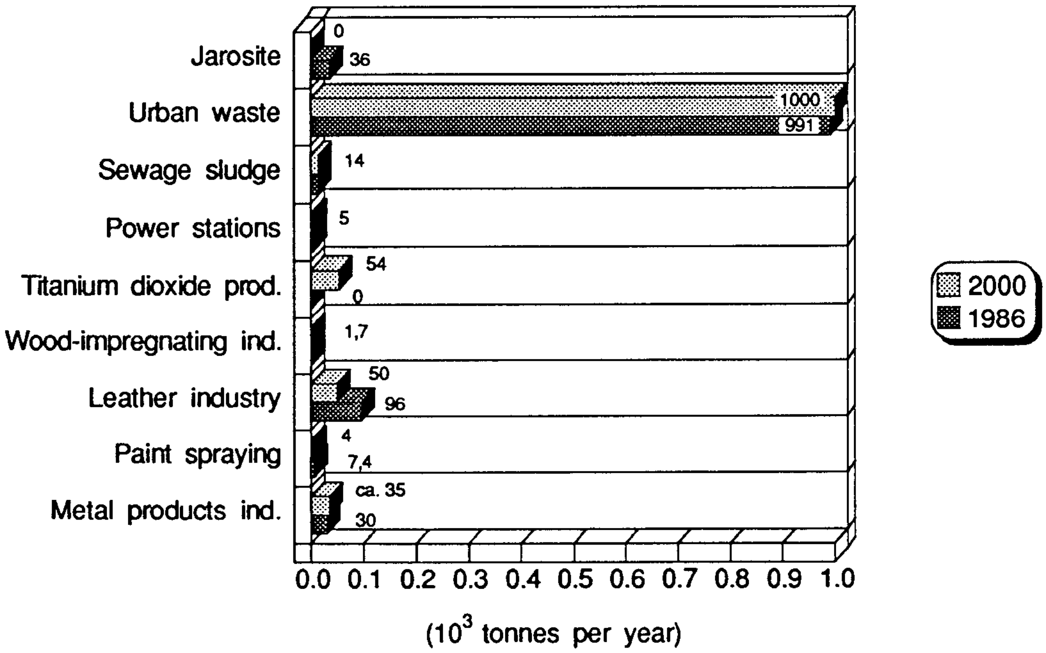


Figure 6.4. *Chromium input to wastes in 1986 and that expected around the year 2000*

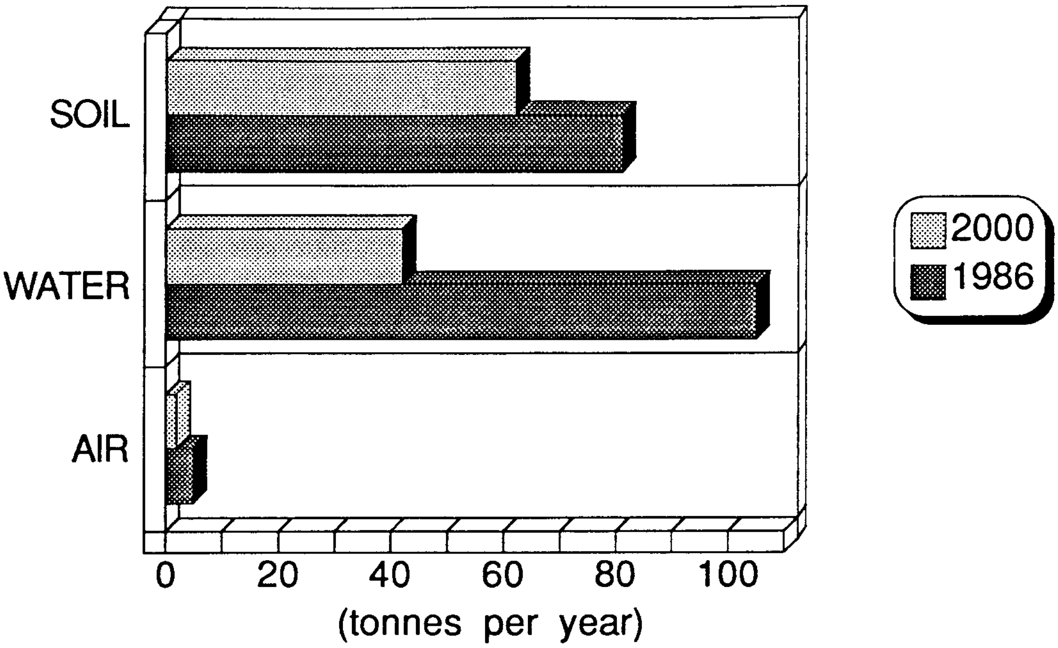


Figure 6.5. Total chromium emissions into air, (fresh) surface water and soil (diffuse) in 1986 and those expected around the year 2000

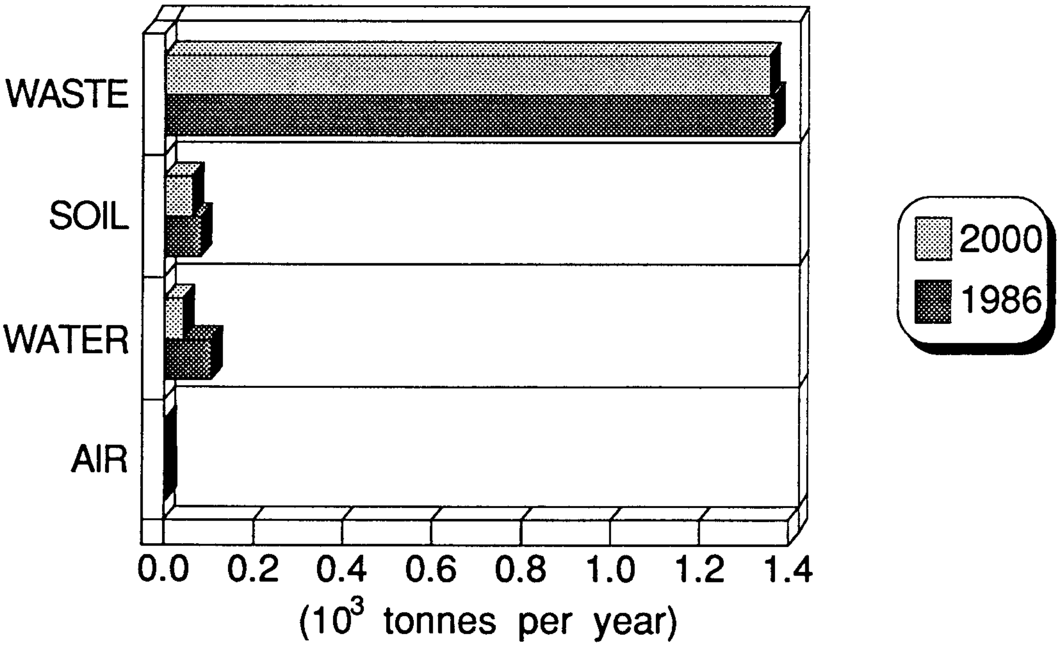


Figure 6.6 As figure 6.5, but including the input to wastes

Table 6.3. *Summary of the implications of the measures to be taken (on the basis of the autonomous developments) for the emission of chromium*

Source	*Measure*	*Chromium emission (tonnes per year)*					
		AIR		*WATER 1)*		*SOIL 2)*	
		1986	*2000*	*1986*	*2000*	*1986*	*2000*
Metal products industry	*process-integrated recovery techn., wastewater purification*	*<0.3*	*<0.25*	*9.9*	*<3*		
Paint spraying	*standardization*	*0.9*	*0.5*			*8.5*	*4.2*
Leather industry	*pollution abatement, wastewater purification, prescription changes*			*2.5*	*1.4*		
Cooling water	*alternatives*			*≤0.5*	*0*		
Titanium dioxide ore-processing industry	*chloride process*			*60*	*6*		
Phosphate ore-processing ind.	*"clean" phosphoric acid technique, other raw materials*			*16*	*≤16*		
Power stations	*different fuel scenarios, FGD systems*	*0.2*	*0.3*				
Sewage sludge	*incineration, controlled dumping, standardization*		*0.08*	*0.2*	*0.3 3)*	*20*	*≤10*
Urban waste	*increased incineration and reuse, decreased dumping, flue-gas scrubbing, standardization*	*0.8*	*0.3*				
Total expected decrease in emissions		*ca 3*		*ca 63*		*ca 19*	

1) Fresh surface water (after purification)
2) Diffuse chromium load
3) As a result of runoff

7. EVALUATION

7.1. EXCEEDING OF THE CURRENT STANDARDS AND GUIDELINES

7.1.1. Soil and groundwater

In general, the soils in the natural areas and arable regions of the Netherlands meet the reference value for chromium. However, the reference value (100 mg.kg^{-1} dry weight in standard soil) and the test value B for the purpose of further research (250 mg.kg^{-1} dry weight in standard soil) are usually exceeded in water meadows and soils covered with harbour sludge.

The average chromium concentration in groundwater is <1 μg.l^{-1}; therefore, the reference value in force for groundwater (7 μg.l^{-1}) is generally not exceeded. Exceptions are the groundwater in infiltration areas (Veluwe) and the groundwater of soils covered with harbour sludge (Broekpolder). However, the measured maximum Cr concentration did not exceed 5 μg.l^{-1}.

7.1.2. Surface water and sediments

The total chromium concentrations in the State water bodies are much lower than the basic quality (50 μg.l^{-1}) for surface water. The same is true for the regional water bodies. The basic quality is occasionally exceeded, which can always be ascribed to the influence of local discharges.

With regard to the chromium concentrations in sediments, it can be stated that the existing recommended limit value (600 mg.kg^{-1} standard soil) is only locally and occasionally exceeded (e.g. in regional sediments of North Brabant: about 3% of the observations). The existing recommended desirable level (basic quality) for sediment (100 mg.kg^{-1}) is exceeded in nearly all sediments of the State water bodies, but the levels in sediments of regional waters are usually (about 90%) below the 100 mg.kg^{-1} limit. When regional sediments exceed this limit, it is due to chromium discharges, which in principle can be treated, and/or water let in from the main system.

The levels will fall further in the longer term. However, a decrease to below the basic quality level in large parts of the main system of the State waters does not appear likely for the time being.

7.1.3. Air

Standards or tolerable levels have not (yet) been established for the compartment air. It should be noted that the ambient air chromium concentrations in the Netherlands are lower than those in West Germany and Belgium.

7.2. RISKS AND RISK GROUPS

7.2.1. Risks to man

- Oral exposure

Data on the dietary intake of chromium in the Netherlands are not available. Based on total diet studies conducted abroad, the average dietary intake is estimated to be 100 µg total Cr per day, with a range of 50 to 200 µg total Cr per day. Data on the speciation of chromium in the diet are not available. Based on the speciation of chromium in biological material [organic Cr(III)] and the small contribution of drinking water (containing 0.1-0.8 µg total $Cr.l^{-1}$ in the Netherlands) to the chromium level in the total diet, it is assumed that the chromium in the diet is mostly present as organic Cr(III). Therefore, the maximum intake of 200 µg total Cr per day corresponds to 0.83 µg absorbed $Cr(III).kg^{-1}$ body weight per day, based on a fractional absorption of 25% and a body weight of 60 kg. The no-effect dose determined in two long-term animal experiments (125 and 6000 µg absorbed $Cr(III).kg^{-1}$ body weight per day, respectively) are 150 times and 7000 times respectively higher than the maximum human intake of 0.83 µg absorbed $Cr(III).kg^{-1}$ body weight per day. Because of these "margins of safety", adverse effects are not expected to occur at the current exposure levels. It should be noted that, in view of the speciation of chromium in surface water in the Netherlands, it cannot theoretically be excluded that chromium in drinking water may be partly present as Cr(VI). This Cr(VI) will be partly reduced to Cr(III) in the stomach; quantitative data on this conversion are not available. The available animal data on Cr(VI) exposure are too limited for a risk assessment for man.

Cr(III) occurs naturally and is an essential trace element for man. The minimum daily requirement is estimated at 0.03-0.13 µg $Cr(III).kg^{-1}$ body $weight.day^{-1}$. It is estimated that the average daily dietary intake is 1.6

μg Cr(III).kg^{-1} body weight, with a range of 0.8 to 3.2 μg Cr(III).kg^{-1}body weight.day^{-1}. Since the estimated minimum daily intake is higher than the upper limit of the minimum daily requirement, adverse effects due to chromium deficiency are not expected at the current exposure levels.

- Exposure by inhalation

A distinction should be made between exposure by inhalation to Cr(VI) and Cr(III). Cr(VI) is considered to be a genotoxic carcinogen, and Cr(III) is not.

It is estimated that exposure to Cr(III) by inhalation results in a maximum daily intake of 0.06 μg, assuming a respiration volume of 12 m^3 per day and a maximum airborne Cr(III) concentration of 5 ng.m^{-3}. This is less than 0.1% of the dietary intake. Based on these data, toxic effects of Cr(III) are not expected at the current exposure levels.

With regard to Cr(VI), the WHO (1987) procedure for estimating its carcinogenic potency was adopted. A risk of 10^{-6} (one extra case of lung cancer per million persons) was calculated for lifelong exposure by inhalation to 0.025 ng Cr(VI).m^{-3}, without differentiating between different Cr(VI) compounds. This corresponds roughly to a risk of 10^{-8} per year, which is considered negligible within the current standardization policy in the Netherlands. The maximum permissible level is 100 times higher, i.e. 2.5 ng Cr(VI).m^{-3}.

The Cr(VI) levels to which the Dutch population is exposed are not known; the current analytical methods are inadequate for determining the speciation of chromium in air. Estimates of the Cr(VI) fraction in ambient air range from 0.01 to 30%. Assuming a national average total Cr level of 2.7 ng.m^{-3}, Cr(VI) could account for 0.0003 to 0.8 ng.m^{-3}. If the highest national total Cr level (5 ng.m^{-3}) were also to obtain regionally, then the Cr(VI) fraction could range between 0.0005 and 1.5 ng.m^{-3}. This means that the "negligibility level" is possibly exceeded both nationally and regionally, but that the levels stay below the maximum permissible concentration. On a local scale, specific Cr(VI) sources may contribute an additional 5 ng Cr(VI).m^{-3} inside a zone of several hundred metres around these sources; in these cases the exposure level varies between about 5 and 6.5 ng Cr(VI).m^{-3}, so that the maximum permissible concentration is exceeded. The risk group comprises an estimated 5,000 to 50,000 persons.

7.2.2. Risks to ecosystems

- Aquatic environment

For the aquatic environment, a value of 7 $\mu g.l^{-1}$ as dissolved Cr [Cr(VI) plus Cr(III)] was calculated using the method of extrapolation proposed by the Health Council (1987), which, in accordance with the risk philosophy of the current standardization policy, can be equated to a draft limit value. This concentration corresponds roughly to a total Cr level of 50 $\mu g.l^{-1}$. This level is not, or no longer, exceeded in both State and non-State water bodies, except in local situations, which can be ascribed to occasional chromium discharges. Based on the current exposure levels in both fresh and sea water, adverse effects on aquatic organisms are not expected.

- Terrestrial environment

The available toxicological data are insufficient for establishing a scientifically underpinned toxicological recommended value. Based on the available information, it is concluded that soil total chromium concentrations up to 100-200 $mg.kg^{-1}$ dry weight (level dependent on clay (particle size < 2 μm) content) do not result in irreversible effects. The concentrations in Dutch soils are generally lower (approximately 10-120 $mg.kg^{-1}$). Only in water meadows and polders covered with harbour sludge are high levels (approximately 100-500 $mg.kg^{-1}$) occasionally observed and ecotoxic effects not excluded.

7.3. ENVIRONMENTAL QUALITY OBJECTIVES

7.3.1. Soil and groundwater

A concentration of 7 $\mu g.l^{-1}$ dissolved Cr was calculated as the draft limit value for surface water, which corresponds roughly to the current basic quality of 50 $\mu g.l^{-1}$ total Cr. This value is higher than the concentration of 2.5 $\mu g.l^{-1}$ dissolved Cr proposed by DBW/RIZA (DBW/RIZA, 1989: Prospects for aquatic organisms), and also higher than the value which is obtained if an improved method of extrapolation is applied to the same set of data: 5 $\mu g.l^{-1}$ dissolved Cr (Van de Meent et al., draft RIVM report: First step towards a system of ecotoxicological risk limits for water and soil).
Since chromium occurs naturally in the environment, a draft desirable level cannot be derived by dividing a draft limit value by a factor of 100 (in

accordance with the risk philosophy of the current standardization policy). It is proposed to use the natural background levels as the desirable value, i.e. 1 $\mu g.l^{-1}$ for fresh surface water and 0.5 $\mu g.l^{-1}$ for salt surface water.
The standard for sediments could possibly be derived from that proposed for surface water. Based on an empirically determined average K_d of 300 x 10^3 $l.kg^{-1}$ and a correction factor for the clay content of 2/3, a draft limit value of about 1400 $mg.kg^{-1}$ could be calculated for sediments. This is a relatively high level, compared with:

(a) the current concentrations in sediments (approximately 50-400 $mg.kg^{-1}$),

(b) the test values for the assessment of the concentrations in soils (table 1.2.: A value 50 + 2C; B value 250; and C value 800 $mg.kg^{-1}$ dry weight), and

(c) the indicative no-effect levels for terrestrial ecosystems, i.e. 200 $mg.kg^{-1}$ dry weight.

As has been mentioned, there are insufficient ecotoxicological data on soil for establishing an effect-oriented standard. The available data seem to support the current reference value (see table 1.2.). From the point of view of public health with respect to food contamination,too, the risk levels do not call for a tightening of the current formulation of standards and guidelines.

Within the integral standardization framework, the recommended value for surface water would also apply to groundwater: 7 $\mu g.l^{-1}$. Owing to a lengthy stay in an anaerobic environment, chromium will be present chiefly in the form of Cr(III), and as such pose no threat to man (drinking water) or the environment. This value is higher than the current reference value (1 $\mu g.l^{-1}$, natural concentration).

Although in the context of an integral approach to the establishment of standards the most critical concentration values in an environmental compartment are determinative of the levels in the other environmental compartments, the question arises whether, in view of the above-mentioned discrepancies, the chosen method of calculation can be used in this case. This discussion will be continued in the afore-mentioned draft RIVM report (Van de Meent et al., 1989).

7.3.2. Air

Unlike the situation in soil and water, the speciation of chromium in air is very important for setting an effect-oriented standard. The principal chromium species in air is Cr(VI) for which draft limit and tolerable values of 2.5 and 0.025 $ng.m^{-3}$, respectively, can be calculated based on the current policy premises. Since there is at the moment no satisfactory method for determining the actual Cr(VI) fraction in ambient air, the practical significance of such a procedure is (as yet) very limited.

7.4. MEASURING STRATEGIES

With regard to soil and groundwater, a general measuring strategy is considered to be of limited use, because (a) the concentrations are generally known, and (b) there are no reasons for supposing that there will be a significant unfavourable change in these concentrations in the near future.
The (eco)toxicological data on surface water do not call for an environmental quality criterion different from the basic quality currently in force. The national measurement programme is considered to be ample. Measurements on sediments can be made at the same locations, for which a lower measuring frequency suffices.

With regard to air, further research is required before a measuring strategy can be developed. This research should be aimed at the Cr(III)/Cr(VI) speciation in air, involving:

a) the development of an analytical method for measuring this speciation,
b) the establishment of the (possible) relationships between Cr(VI) sources and the ambient air Cr(VI) concentrations, and
c) the establishment of a (possible) relationship between the presence of (high concentrations of) photo-oxidants and of elevated Cr(VI) concentrations in the ambient air.

7.5. FEASIBILITY OF ENVIRONMENTAL QUALITY REQUIREMENTS

The concentration values in the Dutch environment are determined to a considerable extent by foreign emissions. Consequently, the effect of autonomous developments and (possible) nation-wide measures is very limited at a national level.

Regarding soil, the indicative no-effect level and the test value B are currently exceeded only in the water meadows and polders covered with harbour sludge. A change in this situation can be expected only in the longer term, through sedimentation in the water meadows of sludge in which the Cr level has decreased and will fall still further in the future. Since for surface water and sediments the proposed and existing environmental quality requirements are the same, the reader can be referred to 7.1.2. for further information. The line of reasoning for sediments is analogous to that for the soil of water meadows. It is assumed that emission-control measures will also be taken on a European level, which will lead to a reduction in the total chromium concentrations in the water of the Rhine and Meuse Rivers. Given the uncertainty in the level of this reduction as well as with respect to the K_d value to be used, it is not as yet possible to give further information on this matter. A decrease to below the reference value cannot be expected for the time being.

Draft limit and tolerable values of 2.5 and 0.025 Cr(VI).m^{-3}, respectively, were proposed for air. It was stated in 7.2. on the basis of estimates that at present the draft tolerable level is possibly exceeded nationally and that locally the draft limit value is exceeded with great certainty. Because of the autonomous developments at the relevant chromium emitters, it is expected that in the year 2000 the draft limit value will no longer be exceeded.

7.6. CONCLUSIONS AND RECOMMENDATIONS

The risks associated with the presence of chromium to man and the environment cannot be adequatuely assessed on the basis of the available data, but they appear to be limited, both at present and in the future.

For man, the range of chromium concentrations ingested in food and drinking water meets the minimum daily requirement and does not exceed the toxicologically maximum acceptable concentration. The ambient air chromium concentrations are generally so low that the maximum permissible levels (in accordance with the philosophy of the standardization policy concerning risk acceptation) are not exceeded; it cannot even be ruled out that at present the concentrations already lie below the level considered to carry a negligible risk to humans. Only in the vicinity (tens to hundreds of metres) of Cr(VI)-emitting sources is the population possibly exposed to levels which exceed the maximum acceptable concentration. In view of the autonomous developments, however, it can be expected that within ten years these local emissions will be so reduced that the levels will nowhere be exceeded.

The concentrations in both fresh- and salt-water ecosystems are generally so low that adverse biological effects are not expected. Soil chromium concentrations are also below the level harmful to terrestrial organisms, except in some water meadows and polders covered with harbour sludge, where ecotoxic effects cannot be excluded. In the long term, however, the Cr concentrations in surface waters, and thereby the Cr levels in sediments and water meadows, will fall further because of emission reductions abroad. In view of the uncertainties as to the chromium problem, various studies can be recommended. As indicated in 7.4., research into the speciation of chromium in air takes priority. In addition, the speciation of chromium in the human diet (especially drinking water) merits further attention.

8. REFERENCES

8.1. REFERENCES CHAPTER 1

DGM (1988)
Normstelling toepassing gereinigde grond
Concept discussienotitie
DGM/DWB/Hoofdafd. Bodem, March 1988
DBW/RIZA (1989)
"Kansen voor Waterorganismen"
Een ecotoxicologische onderbouwing voor kwaliteitsdoelstellingen voor water en waterbodem
Deel 1. Resultaten en berekeningen
DBW/RIZA nota nr. 89.016a
EEC (1975)
Publicatieblad van de Europese Gemeenschappen, no. L 194/38
EEC (1979)
Vereiste kwaliteit van schelpdierwater
Publicatieblad van de Europese Gemeenschappen, no. L 281/50
EEC (1980a)
Richtlijn van de Raad, van 17 december 1979, betreffende de bescherming van het grondwater tegen verontreiniging veroorzaakt door de lozing van bepaalde gevaarlijke stoffen
Publicatieblad van de Europese Gemeenschappen, no. L 20/43
EEC (1980b)
Richtlijn van de Raad, van 15 juli 1980, betreffende de kwaliteit van voor menselijke consumptie bestemd water
Publicatieblad van de Europese Gemeenschappen, no. L 229, 30 augustus 1980
EEC (1982)
Publicatieblad van de Europese Gemeenschappen, no. C 17617
EEC (1988a)
Verslag EG-deskundigenoverleg betreffende chroom in zuiveringsslib in de landbouw, 5 februari 1988 te Brussel (richtlijn 86/278/EG)
F. Folkertsma, DBW/RIZA, 11 maart 1988
EEC (1988b)
Voorstel voor een richtlijn van de Raad betreffende kwaliteitsdoelstelling voor water ten aanzien van chroom
Brussel, 5 februari 1988
EPA (1981)
Biological monitoring of toxic trace elements - Project Summary
Environmental Monitoring Systems Laboratory, Las Vegas, Nevada
EPA-600/S3-80-090
EPA (1984)
Health assessment document for chromium, final report
EPA-600/8-83-014F, August 1984
Food and Drugs Act (1980)
Cosmeticabesluit
Stbl. 1980, 256
Holleman, A.F. and E. Wiberg (1985)
Lehrbuch der Anorganischen Chemie
W. de Gruyter, New York, pp. 1081-1095
IAWR (1986)
Rijn-memorandum 1986
ISBN 90 70671 04 2

IDC (1985)
Overzicht normen luchtkwaliteit, MIC-waarden
3de aanvulling maart 1985
Interprovinciaal Documentatie Centrum
IMP-Water (1984)
Indicatief Meerjarenprogramma Water 1985-1989
Tweede Kamer, vergaderjaar 1984-1985, 19153, nrs. 1-2
IRPTC (1978)
Data Profile on Chromium
Krauskopf, K.B. (1979)
Introduction to geochemist, 2nd ed. McGraw Hill, pp. 545
Leegwater, D.C. et al (1985)
Review of literature data on chromium
VROM, september 1985
MPV-88 (1987)
Milieuprogramma 1988-1981, voortgangsrapportage
Tweede Kamer, vergaderjaar 1987-1988, 20202, nrs. 1-2
MPV-88 (1987)
Milieuprogramma 1989-1989, voortgangsrapportage
Tweede Kamer, vergaderjaar 1988-1989, 20803, nrs. 1-2
NAS (1974)
Chromium
Report of the Subcommittee on Chromium, Committee on Biological Effects of Atmospheric Pollutants
National Academy of Sciences, Washington, D.C.
NAS (1980)
Recommended dietary allowances
9th. rev. ed. Food and Nutrition Board
National Academy of Sciences, Washington, D.C.
National MAC-list (1986)
Directoraat Generaal van de arbeid
Voorburg
NRC (1980)
Recommended dietary allowances, 9th ed.
National Research Council, Food and Nutrition Board, National Academy of Sciences, Washington
Nriagu, J.O. and E. Nieboer (1988)
Chromium in the natural and human environments
Wiley & Sons, New York
SCMO-TNO (1977)
Milieunormen en criteria
Delft
Staatsblad 435 (1977)
Bijlagen van het Koninklijk besluit van 26 mei 1977 tot uitvoering van artiek 1, eerste en derde lid, van de Wet chemische afvalstoffen
Staatsblad 606 (1983)
Besluit van 3 november 1983, houdende regelen inzake kwaliteitsdoelstelling en metingen oppervlaktwateren
TA-Luft (1986)
Technische Anleitung zur Reinhaltung der Luft Erste Allgemeinen Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz, 1974
Geändert durch Verw. - Vorschrift vom 27 Februar 1986
TDB (1985)
Toxicological database
Online file, 1985

Unie van Waterschappen (1985)
Richtlijn voor de afzet van zuiveringsslib ten behoeve van het gebruik op bouw- en grasland, augustus 1985
USEPA (1984)
Summary of published Acceptable Daily Intakes for EPA's Priority Pollutants, internal review draft
ECAO-CIN-437, April 1984
VROM (1986)
Richtlijn voor de inhoud van het provinciaal plan voor de verwijdering van zuiveringsslib
VROM-DGMH-AST, February 1986
VROM (1987)
Concept Leidraad Bodemsanering
Leidschendam
Water Board Decree (1984)
Staatsblad 345, 7 juni 1960, inclusief wijzigingen in werking getreden op 1 juli 1984
Weast, R.C. (1975)
Handbook of chemistry and physics (56th ed.)
The chemical Rubber Publ. Comapny, Cleveland, Ohio
WGD (1985)
Grenswaarden Chroom en Chroomverbindingen
Uit: Reeks Gezondheidkundige adviezen van de Werkgroep van Deskundigen ter vaststelling van MAC-Waarden
RA 6/85
Werkgroep Normering (1986)
Interimrapport van de Werkgroep Normering
Onderwaterbodemoverleg RWS/DGMH, maart 1986
WHO (1987)
Air quality guidelines
ISBN 92-890-1114-9
Zielhuis, R.L. (1981)
Chemische drinkwaterkwaliteit: normstelling en waarden
H_2O, 14, 290-296

8.2 REFERENCES CHAPTER 2

Beker, D. (1988)
Emissions from landfills
RIVM rapport no. 738605004
Berbee, R. (1987)
Relatie diffuse vervuilingsbronnen en waterbodems
Studiedag "waterbodemvervuiling" van het Nederlands Studie Centrum, 24 april 1987, Rotterdam
Berenschot/Tebodin (1987)
Bedrijfstakgewijze milieustudie kunstmeststoffenindustrie: deelrapportage fosforzuurproducenten
Opdracht van Ministerie van VROM
Bolt, N. (1985)
Toepassingen en milieu-aspecten van vliegas
Verslag CMZ-Milieudag, 22 mei 1985
Bolt, N. and A. Snel (1985)
Milieu-aspecten van vliegastoepassingen
Energiespectrum, 11, 321-333

Bolt, N. (1983)
Het uitlooggedrag van drie bodemassoorten en drie vergelijkbare wegfunderingsmaterialen
KEMA, Arnhem
Broers & Partners (1988)
Marktperspectief onderzoek + financieel-economische analyse houtimpregneerbranche
Opdracht van NEHEM, rapport no. DJK/JKF/hr, Baarn
CBS
Personal Communication Van Cruchten, Olsthoorn and Meeuwissen
Voorburg
CBS (1985)
Fosfor in Nederland 1970-1983
Staatsuitgeverij Den Haag
CBS (1986)
Maandstatistiek van de buitenlandse handel per goederensoort
Jaargang 37, no. 12, Staatsuitgeverij Den Haag
CBS (1987)
Waterkwaliteitsbeheer. Deel b. Zuivering van afvalwater 1984
Staatsuitgeverij Den Haag
CBS (1988a)
Waterkwaliteitsbeheer. Deel b. Zuivering van afvalwater 1985
Staatsuitgeverij Den Haag
CBS (1988b)
Koper in Nederland 1985
CBS milieustatistieken
Staatsuitgeverij, Den Haag
DBW/RIZA (1986)
Feenstra, F.J. and P.F.J. van der Most
CUWVO VI: subwerkgroep diffuse bronnen van waterverontreining.
Instituut Milieuvraagstukken. Rapport E-85/15, Amsterdam
DBW/RIZA (1988)
Afvalwaterproblematiek van de textielveredelingsindustrie
CUVWO VI
Department of Public Works (Rijkswaterstaat) (1980-1986)
Kwaliteitsonderzoek in de rijkswateren 1980-1986. Lelystad
DHV (1988)
Afvalwaterproblematiek van de textielveredelingsindustrie
CUVWO VI
DHV (1988)
Diffuse bronnen van waterverontreiniging in het Rijnstroomgebied (exclusief af- en uitspoeling van niet-verharde oppervlakken)
Inventarisatie en kwantificering ten behoeve van het Rijnactieprogramma (actiepunt A4; onderdeel diffuse bronnen)
Opdracht van DWB/RIZA, Rapport C-0266-10-001, Amersfoort
Dijkzeul, A. (1979)
De afgifte van zware metalen en fluoride door diverse oeverbeschermingsmaterialen
DWB/RIZA, Lelystad
Hartford W.H. (1979)
"Chromium compounds" In Encyclopedia of Chemical Technology
Wiley & Sons Publ., New York, volume 6, pp. 82-120
Haskoning (1988)
Interimrapport voor het hoofdstuk twee (productie, toepassingen, bronnen en emissies) van het basisdocument chroom en chroomhoudende stoffen
Opdracht van het RIVM
Nijmegen

IARC (1980)
Chromium and chromium compounds
IARC. Monographs on the evaluation of the carcinogenity of chemicals to humans. Some metals and metal compounds
Lyon Intern. Agency Res. Cancer, 23, pp. 205-323
IMP Water (1980-1984)
Indicatief Meerjaren Programma Water
Ministerie van VROM, Den Haag
IMP Water (1985-1989)
Indicatief Meerjaren Programma Water
Ministerie van VROM, Tweede Kamer vergaderjaar 1984-1985, 19 153, no. 1-2,
Den Haag
IRPTC (1987)
International Register for Potentially Toxic Chemicals
Data profile on chromium, Geneve
Jaarsveld, J.A. van, R.M. van Aalst and D. Onderdelinden (1986)
Deposition of metals from the atmosphere into the North Sea: model calculations
RIVM, report no. 842015002, Bilthoven
KEMA (1988)
Meij, R.
Chroomstromen bij electriciteitscentrales
KEMA rapport, Arnhem
Kirk & Othmer (1978-1982)
Encyclopedia of Chemical Technology, 3rd edition, 1978-1982
Landbouw Economisch Instituut/CBS (1987)
Landbouwcijfers, Den Haag
Martens, W.G. (1986)
Produktie, samenstelling en afzet van zuiveringsslib afkomstig van de particuliere zuiveringsinrichtingen in Nederland in 1982 en 1983
H_2O, 9, 188-190
NEHEM (1986)
Raaf, A.J. de en G.F.A. Klappe
Voorverkenning naar de mogelijkheden voor structuurverbetering van houtimpregneerbedrijven in Nederland
Den Bosch
Nriagu, J.O. and Nieboer (eds) (1988)
Chromium in the Natural and Human Environment
Wiley & Sons Publ., New York
Pacyna, J.M. and J.O. Nriagu (1988)
Atmospheric emissions of chromium from natural and anthropogenic sources
In: Nriagu & Nieboer (eds.): Chromium in the Natural and Human Environment
Wiley & Sons Publ., New York, pp. 105-124
PEO (1986)
Air pollution as a result of the emission from coal-fired power stations
National Coal Research Programme
Stichting Projectbeheerbureau Energieonderzoek (PEO)
Project no. 20.70-004.11, Utrecht
Provincie Noord-Brabant (1988)
Personal communication from mrs. Gelms concerning research leather industry
Den Bosch

RIVM (1985a)
Anthonissen, I.H., H.J. Bremmer, P.J. Meijer, B.L. van der Ven en S.F. van der Weide
Inventarisatie van kleine hoeveelheden (< 20 ton/jaar) chemisch afval en probleemstoffen naar soorten en bronnen van ontstaan (deelproject 3 van het project Klein Chemisch Afval)
RIVM Rapport no.851901001, Bilthoven
RIVM (1985b)
Vogelvluchtverkenning grafische industrie, Bilthoven
RIVM (1987a)
Bremmer, H.J., J.M. Joosten, P.J. Meijer, A.A. Sein, J.J. Sluijmers, E.R. Soczo en R.J. Swart
Ontwikkelingen in hoeveelheden van enkele afvalstoffen en hun verwerking
RIVM Rapport no. 73860503, Bilthoven
RIVM (1987b)
Cornelissen, A.A.J.
Sorteerproeven met huishoudelijk afval, resultaten 1986
RIVM rapport no. 738505002, Bilthoven
RIVM (1988)
Siemons, J.A.E.M.
De afvalverbranding in 1986
RIVM Rapport no. 738605004, Bilthoven
RIZA
Personal communication from mr. Berbee, Lelystad
Ros, J.P.M. (1985)
Beoordelingssysteem nieuwe stoffen. Onderdeel: uitworpverwachting textielkleurstoffen
RIVM rapport no. 851502001, Bilthoven
Slooff, W, R.F.M.J. Cleven, J.A. Janus and J.P.M. Ros (1987)
Basisdocument Koper
RIVM, rapport no. 758474003, Bilthoven
Sloot van der, H.A., J. Wijkstra, A. van Dalen, H.A. Das, J. Slanina, J.J. Dekkers and G.D. Wals (1982)
Leaching of trace elements from coal solid waste
ECN-rapport 82-1020, Petten
Sloot van der, H.A., J. Wijkstra, C.A. van Stigt and D. Hoede (1985)
Leaching of trace elements from coal-ash and coal-ash products
In: Duedalli, Kester & Park (eds.). Wastes in the Ocean. Volume 4: Energy Wastes in the Ocean, Wiley & Sons Publ., New York
SRI (1985)
Specific information on chromium
Meno Park, California
Starkenburg, W.J. van and A.B. van Luin (1985)
Anorganische en organische microverontreinigingen in industrieel afvalwater, een inventarisatie
DWB/RIZA rapport no. 8611, Lelystad
State of California (1986)
Public hearing to consider the adoption of a regulatory amendment identifying hexavalent chromium as a toxic air contaminant
Agenda item no. 86, January 24, 1986
Stichting Natuur en Milieu (1986)
A. Klingenberg
Grafische chemicaliën. Stoffengebruik, emissies, werkomstandigheden, schone technologie
Opdracht van Ministerie van VROM, Utrecht

Stiepelman, H., B. Daimler, H. Tieben en F. Aumann (1981)
Recycling in der Textilwirdschaft
TAUW (1984)
Slakken en Vliegassen. Milieuhygiënische aspekten en toepassingsmogelijk heden van slakken en vliegassen afkomstig van huisvuilverbrandingsinstallaties (samenvattende rapportage)
Rapport no. 51166.01/RO-08, Deventer
Tebodin (1984)
De uitloging van creosootolie en koperchroomarseen en koperchroom uit geïmpregneerd hout
Rapport in opdracht van vereniging van houtimpregneerinrichtingen in Nederland
Referentie WB/LK, Den Haag
TNO (1981)
Doorgeest, T.
Het grondstoffenverbruik van de Nederlandse Verfindustrie en enige milieuhygiënische consequenties
TNO, V-81-X, Delft
TNO (1985)
Vogelvluchtverkenning. Leder-, Schoen- en andere Lederwarenindustrie
Project bedrijfsafvalstoffen
Opdracht van het RIVM, opdracht no. 1001 34 573, Delft
TNO (1986)
Uitloging van creosoot en CCA uit geïmpregneerd hout
Opdracht van DWB/RIZA
Referentie HI 86.1002/DONGI/LM, Delft
TNO (1987)
Dongen, van P.
Uitloogkarakteristieken van verduurzaamd hout in de opslagfase, deel 1 en 2
Opdracht van ministerie van VROM, Rapport no. HI 87.11.78, Delft
Udo de Haes, H.A., G. Hupkes and G. Guinnee (1988)
Stofbalansen en stroomschema's: de accumulatie van stoffen in economie en milieu
Milieu, 2, 51-55
Vellinga, T., J.P.J. Nijssen and J. Dogterom (1988)
Schoon havenslib door en schone Rijn
H_2O, 6, 134-137
Vliegasunie (1986)
Jaarverslag 1986, Den Bosch
VROM (1988a)
Gegevensverzameling in het kader van artikel 22 Wet milieugevaarlijke stoffen: interne rapportage chroom(VI)verbindingen. Uitgevoerd door TAUW Infra Consult B.V., Rapport 142-660/UW/esk, Deventer
VROM (1988b)
Uitdraai emissieregistratie, eerste en tweede ronde, Den Haag
VROM (1988c)
Informatiebundel leder-, schoen- en andere lederwarenindustrie
Handhaving Milieuwetten no. 20., Staatsuitgeverij Den Haag
VVVF (1987)
Jaarverslag van de Vereniging van Verf- en Drukinktfabrikanten, Wassenaar
VVVF
Personal communication from mr. de Jonge, Wassenaar
World Bureau of Metal Statistics (1987)
Chromium

8.3. REFERENCES CHAPTER 3

Air Resources Board (1986)
Public hearing to consider the adoption of a regulatory amendment identifying hexavalent chromium as a toxic air contaminant, State of California
Angus, J.C., Bei Lu and M.J. Zappia (1987)
Potential-pH diagrams for complex systems
J. Appl. Electrochem., 17, 1-21
Baes, C.F. and R.E. Mesmer (1977)
The hydrolysis of cations
Wiley-Interscience, New York, 211-220
Bartlett, R.J. and J.M. Kimble (1977)
Behavior of chromium in soils. I. Trivalent forms
J. Environ. Qual., 5, 379-383
Bartlett, R.J. and B.R. James (1979)
Behavior of chromium in soils. III. Oxidation
J. Environ. Qual., 8, 31-35
Boer, J. de (1989)
Personal communication, RIVM
Bolt, G.H. and M.G.M. Bruggenwert (1976)
Soil chemistry. A. Basic elements
Elsevier, Amsterdam
Boyko, S.L. and D.M.L. Goodgame (1986)
Inorg. Chim. Acta, 123, 189-191
Cary, E.E. (1982)
Chromium in air, soil and natural waters
Biological and Environmental Aspects of Chromium (Langård, S., Ed.), Elsevier Biomedical Press, Hoofdstuk 3, 49-64, Amsterdam
Cotton, F.A. and G. Wilkinson (1980)
Advanced Inorganic Chemistry
John Wiley & Sons, New York, 719-749
DBW/RIZA (1982)
De Waterkwaliteit van de Rijn 1970/1981
Nota 82/061, Dijkzeul A.
Frissel, M.J., P. Poelstra, and P. Reiniger (1975)
in: The Behaviour of Chromium in Aquatic and Terrestrial Food Chains
EUR 5375e, Luxembourg, pp. 27-42
Garrels R.M. and C.L. Christ (1965)
in: Solutions, Minerals and Equilibria (Croneis, C., Ed.), Harper & Row, N.Y., p. 381
Goh C.L., P.H. Wong, S.F. Kwok and S.L. Gan (1986)
Chromate allergy: total chromium and hexavalent chromate in the air
Dermatosen 34, 132-134.
Griffin, R.A., A.K. Au and R.R. Frost (1977)
Effect of pH on adsorption of chromium from landfill leachate by clay minerals
J. Environm. Sci. Health, A12, 431-449
Grim, R.E. (1986)
Clay mineralogy
McGraw-Hill, New-York
Grove, J.H. and B.G. Ellis (1980)
Extractable chromium as related to soil pH and applied chromium
Soil Sci. Soc. Am. J., 44(2), 238-242

Hem, J.D. (1977)
Reactions of metal ions at surfaces of hydrous iron oxide
Geoch. Cosm. Acta, 41, 527-538
Huffman, E.W.D.,Jr. (1973)
Chromium, Essentiality to plants. Forms and distribution in plants and availability of plant chromium to rats
Ph. D. Thesis, Cornell University
Jaarsveld, J.A. van and D. Onderdelinden (1986)
Modelmatige beschrijving van concentratie en depositie van kolen relevante componenten in Nederland, veroorzaakt door emissies in Europa
James, B.R. and R.J. Bartlett (1983a)
Behavior of chromium in soils. V. Fate of organically complexed Cr(III) added to soil
J. Environ. Qual., 12, 169-172
James, B.R. and R.J. Bartlett (1983b)
Behavior of chromium in soils. VI. Interactions between oxidation-reduction and organic complexation
J. Environ. Qual., 12, 173-176
James, B.R. and R.J. Bartlett (1983c)
Behavior of chromium in soils. VII. Adsorption and reduction of hexavalent forms
J. Environ. Qual., 12, 177-180
Langård, S. (1982)
Biological and Environmental Aspects of Chromium (Langård, S., Ed.), Elsevier Biomedical Press, Amsterdam
Milford J.B. and C.I. Davidson (1985)
The sizes of particulate trace elements in the atmosphere - a review
J. Air Pollut. Control Assoc., 35, 1249-1260
Musić, S., M. Ristić and M. Tonković (1986)
Sorption of chromium(VI) on hydrous iron oxides
Z. Wasser-Abwasser-Forsch., 19, 186-196
Murrman B.P. and F.R. Koutz (1972)
Role of soil chemical processes in reclamation of waste water applied to land
U.S. Army Corps of Engineers, Cold Regions Research and Engineering Lab., Hanover, N.H.
Nieboer, E. and A.A. Jusys (1988)
Biological Chemistry of Chromium
Chromium in the Natural & Human Environments (Nriagu, J.O. & Nieboer, E., Eds.), Wiley & Sons, 21-79, New York
NRCC (1985)
Chromium Update 1984. Environmental and nutritional Effects of Chromium
National Research Council Canada
Nriagu J.O., J.M. Pacyna, J.B. Milford and C.I. Davidson (1988)
Distribution and characteristic features of chromium in the atmosphere
Chromium in the Natural & Human Environments (Nriagu, J.O. & Nieboer, E., Eds.), Wiley & Sons, 125-172, New York
Nriagu, J.O. and E. Nieboer (1988)
Chromium in the Natural & Human Environments (Nriagu, J.O. & Nieboer, E., Eds.), Wiley & Sons, New York
Pacyna J.M. and J.O. Nriagu (1988)
Atmospheric emissions of chromium from natural and anthropogenic sources
Chromium in the Natural & Human Environments (Nriagu, J.O. & Nieboer, E., Eds.), Wiley & Sons, 105-124, New York

Potma C.J.M., D. Onderdelinden and J. Slanina (1986)
Bijdrage van een kolengestookte electriciteitscentrale aan de lokale luchtconcentratie- en depositieniveaus
RIVM-rapport 228202004
Robertson, F.N. (1975)
Hexavalent chromium in the ground water in Paradise Valley, Arizona
Ground Water, 13, 516-527
RIZA (1988)
Personal communication
Rühling A., L. Rasmussen, K. Pilegaard, A. Mäkinen and E. Steinnes (1987)
Survey of atmospheric heavy metal deposition in the Nordic countries in 1985
The Nordic Counsil of Ministers, Kopenhagen
Salomons, W. (1983)
Trace metals in the River Rhine, their past and present (1920-1983): influence on aquatic and terrestrial ecosystems
Heavy Metals in the Environment, Intern. Conf., Heidelberg. CEP Consultants Ltd, Edinburgh
Schmidt, R.L. (1984)
Thermodynamic properties and environmental chemistry of chromium
Report PNL-4881 UC-1, US Dept. of Energy, contract DE-AC06-76RLO 1830
Schnitzer, M. (1978)
Humic substances: Chemistry and reactions
Soil Organic Matter (Schnitzer M. & Khan, S.U., Eds.) Elsevier, Amsterdam, pp. 1-64 Elsevier
Sengupta, A.K. and D. Clifford (1986)
Important process variables in chromate ion exchange
Environ. Sci. Technol., 20, 149-155
Stern, R.M. (1982)
Chromium compounds: production and occupational exposure
Biological and Environmental Aspects of Chromium (Langård, S., Ed.), Elsevier Biomedical Press, Hoofdstuk 2, 5-48, Amsterdam
RIVM-rapport 228202002.
Stollenwerk, K.G. and D.B. Grove (1985a)
Adsorption and desorption of hexavalent chromium in an alluvial aquifer near Telluride, Colorado
J. Environ. Qual., 14, 150-156
Stollenwerk, K.G. and D.B. Grove (1985b)
Reduction of hexavalent chromium in water samples acidified for preservation
J. Environ. Qual., 14, 396-399
Stumm, W. and J.J. Morgan (1981)
Aquatic chemistry. An introduction emphasizing chemical equilibria in natural waters (2nd ed.)
Wiley-Interscience, New-York
Thomsen, E. and R.M. Stern (1979)
Scand. J. Work Environm. Health, 5, 386-403
Vos G. (1985)
Determination of dissolved hexavalent chromium in river water, sea water and waste water
Z. Anal. Chem., 320, 556-561
ZMAS (1984)
Zware metalen in aquatische systemen - Geochemisch en biologisch onderzoek in Rijn en Maas en de daardoor gevoede bekkens (Hueck-van der Plas, red.)
TNO, Delft

8.4. REFERENCES CHAPTER 4

Air Resources Board (1985)
Procedure for the sampling and analysis of atmospheric total chromium, lead manganese and nickel; Method 105; State of California
Air Resources Board (1986a)
Standard Operating Procedure for the Speciation and Analysis of Hexavalent Chromium at Ambient Atmospheric Levels; Method ADDL006; State of California
Air Resources Board (1986b)
Public hearing to consider the adoption of a regulatory amendment identifying hexavalent chromium as a toxic air contaminant, State of California
AAS, (1980)
Mineral element composition of Finnish foods: N, K, Mg, P, S, Fe, Cu, Mn, Zn, Mo, Co, Ni, Cr, F, Se, Si, Rb, Al, B, Br, HG, As, Cd, Pb and ash
Acta Agriculturae Scandinavica, Stockholm
Aubert, H. and M. Pinta (1977)
Trace elements in soils
Elsevier, Amsterdam
Bignoli, G. and M. Sabbioni (1981)
Long-term prediction of the potential impact of heavy metals on groundwater quality as a result of fertilizers use
Studies in Environm. Sci., <u>17</u>, 857-862
Bom, C.M. (1981)
Evaluation of different analytical procedures in the trace element analysis of a landfill leachate
Quality of groundwater, Studies in Environm. Sci., <u>17</u>, 495-499
Bowen, H.J.M. (1979)
Environmental chemistry of the elements
Acad. Press Inc., London
Brinkman, F.J.J. (1981)
Lekkerkerk
Studies in Environm. Sci., <u>17</u>, 1049-1051
Buchet, J.P., R.Lauwerys, A. Vandevoorde and J.M. Pycke (1983)
Oral daily intake of cadmium, chromium, mercury, calcium, zinc and arsenic in Belgium: a duplicate meal study
Fd. Chem. Toxic, 21 [1], 19-24
CBS (1987)
Waterkwaliteitsbeheer deel a, Lozing van afvalwater 1984
Cleen, M. de and Y. Tieleman (1988)
Elementen op het spoor. Een literatuurstudie naar de bepalende factoren voor achtergrondgehalten aan spoorelementen en een model ter benadering van het chroomgehalte in Nederlandse bodems
LU Wageningen
CUWVO (1980)
Diffuse bronnen van waterverontreiniging
Rapport werkgroep VI
CUWVO (1987)
De waterkwaliteit van Nederland in 1986
Davies, B.E. (1980)
Applied soil trace elements
Wiley-Interscience, New York

DG (1988)
Nota GWWS 88-001
Dienst Getijdenwateren Rijkswaterstaat
DHV (1988)
Diffuse bronnen van waterverontreiniging in het Rijnstroomgebied (exclusief af- en uitspoeling van niet-verharde oppervlakken)
Inventarisatie en kwantificering ten behoeve van het Rijnactieprogramma (actiepunt A4; onderdeel diffuse bronnen)
Opdracht van DWB/RIZA, Rapport C-0266-10-001, Amersfoort
Dijkzeul, A. (1981)
De waterkwaliteit van de Maas 1953-1980
DBW/RIZA nota 81-048, Lelystad
Dijkzeul, A. (1982)
De waterkwaliteit van de Rijn 1970-1981
DBW/RIZA nota 82-061, Lelystad
Driel, W. van, and K.W. Smilde (1981)
Heavy metal content of dutch arable soils
Landwirtsch. Forsch., 38, 305-313
Duijvenbooden, W. van (1981)
Groundwater quality in the Netherlands - collection and interpretation of data
Studies in Environm. Sci., 17
Duijvenbooden, W. van, L.F.L. Gast and J. Taat (1985)
Landelijk Meetnet Grondwaterkwaliteit. Eindrapport van de inrichtingsfase
RIVM Rapport nr. 840382001, Bilthoven
Eck, G.Th.M. van, H. van 't Sant and E. Turkstra (1985)
Voorstel referentiewaarden fysisch-chemische waterkwaliteitsparameters Nederlandse zoute wateren
VROM, Leidschendam
Edelman, Th. (1984)
Achtergrondgehalten van een aantal anorganische en organische stoffen in de bodem van Nederland, een eerste verkenning
VROM - Serie Bodembescherming, 34
Edwards, J.G., S.J. Haswell and C.J. Jackson (1985)
Int. Conf. Heavy Metals in the Environment, Athene, September 1985
CEP Consultants Ltd, Edinburgh, 460-462
Ellen, G., J.W. van Loon and K. Tolsma (1989)
Koper, mangaan, zink, chroom en nikkel in runder-, varkens- en schapenieren en in kuikenlevers
RIVM rapport 388703001
EPA (1981)
Biological monitoring of toxic trace elements
Project summary environmental monitoring systems laboratory, Las Vegas Nevada
EPA-600/s3-80-090
EPA (1984)
Health Assessment Document for Chromium; Final Report
EPA-600/8-83-014F
Facer, J.L. (1983)
Personal communication to Dr. M. Mercier, IPCS (United Kingdom Ministry of Agriculture, Fisheries and Food, London)
Goncharov, A.T. (1968)
Role of chromium in the nutrition of animals and man
Vopr. Pitan., 27, 59-66 (in Russian)

Griepink, B (1984)
Investigation of methods and sources of error in trace element analysis in surface waters using the determination of chromium and mercury as examples
Pure & Appl. Chem, 56, 1477-1498
Guthrie, B.E. (1973)
Daily dietary intakes of zinc, copper, manganese, chromium and cadmium by some New Zealand women
Proc. Univ. Otago Med. Sch., 51, 47-49
Haring, B.J.A. (1984)
Lead in drinking water
Thesis
Harzdorf, A.C. (1987)
Analytical Chemistry of chromium species in the environment, and interpretation of the results
Intern. J. Environm. Anal. Chem., 29, 249-261
IHE (1986)
Evaluatie van de gehalten aan zware metalen in de omgevingslucht in België
Instituut voor Hygiëne en Epidemiologie, Brussel, 6e jaarrapport, ISSN 0773-0284
IMG-TNO (1983)
De belastende agentia en factoren bij het lassen; eindrapport
Rapport IMG-TNO
IMP Water (1985-1989)
Indicatief Meerjaren Programma Water
Ministerie van VROM, Tweede Kamer vergaderjaar 1984-1985, 19 153, no. 1-2,
Den Haag
Jaarsveld, J.A. van and D. Onderlinden (1986)
Luchtverontreiniging ten gevolge van kolengestookte installaties
Stichting Rrojectbeheerbureau Energieonderzoek
projectnummer 20.70-017.11; deelrapport 4
Jochems J.J. (1986)
Rapport betreffende werkplekgegevens en technische/economische mogelijkheden i.v.m. de voorgenomen MAC-verlaging voor chroom en chroomverbindingen
Min. van Soc. Zaken en Werkgel., DG-Arbeid, Voorburg
Kerdijk, H.N. (1981)
Groundwater pollution by heavy metals and pesticides from a dredged spoil dump
Quality of groundwater, Studies in Environm. Sci., 17, 279-286
Kumpulainen, J.T., W.R.Wolf, C. Veillon and W. Mertz (1979)
Determination of chromium in selected United States diets
J. Agric. Food Chem., 27, 490-494
Langård, S. (1982)
Biological and Environmental Aspects of Chromium (Langård, S., Ed.), Elsevier Biomedical Press, Amsterdam
Locatelli, C. and F. Fagioli (1986)
Determination of chromium(VI) in dialysis fluids by alternating current and differential pulse voltammetry
Mikrochim. Acta(Wien) II, 269
Levine, R.A., D.H.P. Streeten and R.J. Doisy (1968)
Effects of oral chromium supplementation on the glucose tolerance of elderly human subjects
Metabolism, 17, 114-125

Lexmond, Th. M. and Th. Edelman (1986)
Voorlopige referentiewaarden en huidige achtergrondgehalten van een aantal zware metalen en arseen in de bovengrond van natuurterreinen en land-bouwgronden
LU Wageningen
MAFF (1985a)
Survey of Aluminium, Antimony, Chromium, Cobalt, Indium, Nickel, Thallium and Tin in Food
The fifteenth report of the steering group on food surveillance; The working party on the monitoring of foodstuffs for heavy metals
United Kingdom Ministry of Agriculture, Fisheries and Food, London
MAFF (1985b)
Survey of aluminium, chromium, cobalt, indium, nickel, thallium and tin in food
Ministry of Agriculture, Fisheries and Food
Food Surveillance Paper No. 15
Merian, E. (1984)
Introduction on environmental chemistry and global cycles of arsenic, beryllium, cadmium, chromium, cobald, nickel, selenium, and their derivatives
Toxicol. Environ. Chem., 8, 9-38
Meulen, A. van der (1987)
Resuspensie van straatstof door verkeer
RIVM rapport 228602003
Misdorp, R. and R. Duijts (1988)
Gehalten aan zware metalen in de bodem van de westelijke Waddenzee in 1987
Moura, M.L. and S.B. Kroonenberg (1988)
Natuurlijke variabiliteit van gehalten aan zware metalen en andere elementen in Kwartaire sedimenten in Zuid-Oost Nederland
Verslag MPW/KOP project
Vakgroep Bodemkunde en Geologie, LU Wageningen, en Rijksgeologische dienst, Haarlem
Murakami, Y., Y. Suzuki, T. Yamagata and N. Yamagata (1965)
Cr and Mn in Japanese diet
J. Radiat. Res., 6, 105-110
NAS (1974)
Chromium
Report of the subcommittee on chromium, Committee on Biological Effects of Atmospheric Pollutants
National Academy of Sciences, Washington D.C,
NAS (1980)
Drinking Water and Health, Vol. 3
National Academy Press, Washington, D.C.
Navrot J. and A.S. Singer (1976)
Soil Sci., <u>121</u>, 337
NEN (1977)
Bepaling van het gehalte aan chroom met behulp van atomaire absorptie-spectrometrie (grafietoventechniek)
NEN 6444, NNI, Delft
NEN (1984)
Het verzamelen van zwevend stof voor de bepaling van het lood- en cadmium-gehalte - HVS-methode; Het verzamelen van zwevend stof voor de bepaling van het gehalte aan metalen
NEN 2785, NNI, Delft

NHW (1980)
Chromium drinking water review
In: Guidelines for Canadian drinking-water quality, 1978. Supporting documentation
Canada, Ottawa, National Health and Welfare, 255-268
Noord-Brabant (1987)
Waterbodems in Noord-Brabant -inventarisatie-
Projectgroep inventarisatie onderwaterbodems
Nriagu, J.O. and E. Nieboer (1988)
Chromium in the Natural & Human Environments (Nriagu, J.O. & Nieboer, E., Eds.), Wiley & Sons, New York
Ros, J.P.M. and Slooff W. (1987)
Ontwerp basisdokument cadmium
RIVM Rapport no. 758476002
Salomons, W. (1981)
Biochemical and hydrodynamical processes affecting heavy metals in rivers, lakes and estuaries
Salomons, W. and A.J. de Groot (1977)
Pollution history of trace metals in sediments as affected by the Rhine river
Environmental Biogeochemistry and Geomicrobiology (Krumbein, W.E., Ed.)
Vol. I, Ann Arbor Science, p. 149
Scalf, M.R. et al. (1981)
Manual of groundwater quality sampling procedures
National Water Well Association
Scheffer, F. and P. Schachtschnabel (1982)
Lehrbuch der Bodenkunde, 11e druk
Ferdinand Enke Verlag
Schelenz, R. (1977)
Dietary intake of 25 elements by man estimated by neutron activation analysis
J. Radioanal. Chem., 37, 539-548
Schlager, R.J. (1984)
Moss landing magnesia and brick plant - Chromium air emissions survey
Kaiser Aluminum & Chemical Corporation
Rapport ZCFT 84-80-RJS
Siebers, H.H. and M. Donze (1984)
Eeen nieuw apparaat om ongeroerde grondmonsters onder water te nemen
H_2O, 17, 74-77
Singh and Van de Meent (1989)
Mathematical Modelling of transfer, transport and transformation of Chemicals in the environment, especially in homo genius multimedical box modelling system
RIVM report no. 768803002
Sjaya, T.P. Rao and G.P. Rao (1986)
Galvanic and potentiometricstripping methods in pollution monitoring of chromium
Bulletin of Electrochemistry, 2, 131-133
Slooff, W., R.F.M.J. Cleven, J.A. Janus and J.M. Ros (1987)
Ontwerp basisdokument koper
RIVM Rapport no. 758474003
Slooff, W. (1987)
Basisdocument Benzeen
RIVM Rapportnummer 758476001
Smart, G.A. and J.C. Sherlock (1985)
Chromium in foods and the diet
Food additives and contaminants, 2, 139-147

Staarink, T. and P. Hakkenbrak (1987)
Contaminantenboekje, een overzicht van stoffen die drink- en eetwaren verontreinigen
Staatsuitgeverij, 's-Gravenhage
Tessier, A., P.G.C. Campbell, J.C. Aucliar and M. Bisson (1984)
Relationship between the partitioning of trace metals in sediments and their accumulation in the tissues of the freshwater mollusc Elliptio complanata in a mining area
Can. J. Fish. Auqat. Sci., 41, 1463-1472
Thijsse, Th. R. and C. Huygen (1985)
Luchtverontreiniging ten gevolge van kolengestookte installaties
Stichting Projectbeheerbureau Energieonderzoek
projectnummer 20.70-012.50; deelrapport 2
Turkstra, E. (1988)
Problematiek verontreinigde waterbodems
WSD-notitie 88-043, DBW/RIZA/Rijkswaterstaat
VPR (1985)
Voorlopige Praktijkrichtlijn Bodem
VPR C 85-01 (concept)
DHV, Amersfoort
VROM (1983)
Invloed van zware metalen op de bodemflora
Serie Bodemberscherming, 20
VROM-L&V-V&W (1985)
Indicatief Meerjaren Programma Milieubeheer 1986-1990
VROM-L&V-V&W (1988)
Milieuprogramma Voortgangsrapportage 1989-1992
VROM-V&W (1985)
Indicatief Meerjaren Programma Water 1985-1989
VROM-V&W (1986)
Rijks Waterkwaliteitsplan
VTCB (1986)
Advies Bodemkwaliteit; Bijlagen bj Advies Bodemkwaliteit
Rapport A86/02-I/II
Voorlopige Technische Commissie Bodembescherming, Leidschendam
Wai, C.M., L.M. Tsay and J.C. Yu (1987)
A two-step extraction method for differentiating chromium species in water
Mikrochim. Acta (Wien), II, 73-78
WHO (1988)
Environmental health criteria, 61, Chromium
World Health Organization, Geneva
WL (1985)
Inventarisatie kwaliteit onderwaterbodems Rijkswateren
Rapport R2120, Waterloopkundig Laboratorium Delft
Waterloopkundig Laboratorium Delft
WL (1987)
Concept-notitie Bronschattingen
Project T0234 'Regulering Stofstromen' i.o.v. DBW/RIZA,
Waterloopkundig Laboratorium Delft
WL (1988)
Microverontreinigingen in sedimenten van de Noordzee
Waterloopkundig Laboratorium Delft
ZMAS (1984)
Zware metalen in aquatische systemen - Geochemisch en biologisch onderzoek in RIJN en MAAS en de daardoor gevoede bekkens (Hueck-van der Plas, red.)
TNO, Delft

Zuid-Holland (1989)
Waterbodems in Zuid-Holland
Werkgroep Waterbodems

8.5. REFERENCES CHAPTER 5

For details and the specific literature consulted, the reader is referred to the appendix: Janus, J.A. and E.I. Krajnc, Appendix to report 758701001, Integrated criteria document chromium: effects (1989).

Gezondheidsraad (1988)
Ecotoxicologische risico-evaluatie van stoffen
Rapport 1988/28, 1988
Kooijman, S.A.L.M. (1987)
A safety factor for LC50-values allowing for differences in sensitivity among species
Water Res., 21, 269-276
Slooff et al. (1986)
Margins of uncertainty in ecotoxicological hazard assessment
Environ. Toxicol. Chem., 5, 841-852
Straalen, N.M. van (1987)
Stofgehalten in de bodem - (geen) effecten op bodemdieren
In: Symposium Bodemkwaliteit, Ede, December 1986
Leidschendam: VTCB, 1987, 75-84

8.6. REFERENCES CHAPTER 6

Bedrijfschap voor de lederindustrie (1988)
Jaarverslag 1987, Tilburg
Bedrijfstakverkenning (1980)
Deel 3a: Leder-, schoen- en andere lederwarenindustrie
Staatsuitgeverij Den Haag
Bohmann, R. (1988)
Complimenten voor de leerindustrie
Handhaving, maart/april 1988, Leidschendam
CBS
Bolt, A., M. Tels and W.J.Th. van Gemert (1984)
Rückgewinnung reiner Metallsalze aus gemischten Schwermetallhydroxyd Schlamm
In: Thome-Kozmiensky (ed.), Recycling International, E. Freitag Verlag für Umwelttechnik Publ., Berlin 1983
Broers & Partners (1988)
Marktperspectief onderzoek + financieel-economische analyse houtimpregneerbranche
Opdracht van NEHEM, rapport DJK/JKF/hr, Baarn
Brugging, J.J.C. et al. (1987)
Nationale energieverkenningen 1987, rapport nr. ESC-42 (Energie Studie Centrum), september 1987
CBS (1988)
Produktiestatistiek van de lederindustrie 1986
Staatsuitgeverij Den Haag
DBW/RIZA (1988)
CUVWO VI: Afvalwaterproblematiek van de textielveredelingsindustrie
't Gilde et al. (1986)
Produktiestatistiek van de lederindustrie 1986
Staatsuitgeverij, Den Haag
ESC (1987)

EZ (1980)
Ministerie van Economische Zaken
Bedrijfstakverkenning 1980, deel IIIa
Leder-, schoen- en andere lederwarenindustrie

Haskoning (1988)
Onderzoek naar de milieu-effecten bij slibverbranding
Rapport in opdracht van de Provincie Zuid-Holland, Nijmegen

IMP Water (1985-1989)
Indicatief Meerjaren Programma Water
Ministerie van VROM, Tweede Kamer vergaderjaar 1984-1985, 19 153, no. 1-2,
Den Haag

IVM/ESI-VU (1980)
Economische aspecten van emissiebeperking: een gemodelleerde aanpak
Ministerie van Economische Zaken

KEMA (1988a)
Meij, R.
Chroomstromen bij electriciteitscentrales, KEMA-rapport ,Arnhem

KEMA (1988b)
Meij, R.
Een prognose van emissies van luchtverontreinigende componenten en produktie van reststoffen ten gevolge van elektriciteitsopwekking bij verschillende scenario's
KEMA-rapport nr. 80183-MOC 88-3216 van 10 juni 1988, Arnhem

Kuijenhoven, L.J. and V.M.G. Mattheij (1986)
Evaluatie onderzoeksprogramma fosforzuurgips
Rapport Tebodin Raadgevende Ingenieurs in opdracht van VROM, Den Haag

Metaalinstituut TNO (1980)
Boose, ir. C.A.
Eindrapport blauwpassiveren, rapportnr. M80/0365 BSE/RAN

NEHEM (1986)
Raaf, A.J. de en G.F.A. Klappe
Voorverkenning naar de mogelijkheden voor structuurverbetering van houtimpregneerbedrijven in Nederland, Den Bosch

Provincie Noord-Brabant (1988)
Personal communication with mrs. Gelms, Den Bosch

Ros, J.P.M. en W. Slooff (1987)
Ontwerp Basisdocument Cadmium
RIVM, rapportno. 758476002, Bilthoven

Ros, J.P.M. (1986)
Berekeningsresultaten met het model galvanisch bedrijf
RIVM-rapport nr. 851401002, Bilthoven

Rijnmond (1985)
Openbaar lichaam Rijnmond. Grootschalige lokatie voor de berging van baggerspecie uit het rivierengebied. Verwerking en nuttig gebruik van onderhoudsbaggerspecie, Rotterdam

Slooff, W, R.F.M.J. Cleven, J.A. Janus and J.P.M. Ros (1987)
Ontwerp Basisdocument Koper
RIVM, rapport 758474003, Bilthoven

State of California (1986)
Public hearing to consider the adoption of a regulatory amendment identifying hexavalent chromium as a toxic air contaminant
Agende item no. 86, January 24, 1986

TA-Luft (1986)
Technische Anleitung zur Reinhaltung der Luft Erste Allgemeinen Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz, 1974
Geändert durch Verw. - Vorschrift vom 27 Februar 1986

Tebodin (1985)
Bedrijfstakgewijze milieustudie houtimpregneerbedrijven, rapport in opdracht van Ministerie EZ en Ministerie VROM, referentie 84166/LK, Den Haag
TNO (1981)
Inventarisatie energieverbruik lederindustrie, Apeldoorn
TNO (1987)
Bedrijfsvoering en afvalstoffen bij de industriële lakapplicatie
TNO-rapport V-87-321, Delft
VOM (1988)
Mogelijkheden van membraanfiltratietechnieken in de natte oppervlaktebewerkende industrie
VOM/TNO-rapport
VOM (1984)
Oppervlaktetechnieken (28), 8, 214-220
VROM (1988a)
Gegevensverzameling in het kader van artikel 22 Wet milieugevaarlijke stoffen: interne rapportage chroom(VI)verbindingen
TAUW Infra Consult B.V., Rapport 142-660/UW/esk, Deventer
VROM (1988b)
Notitie inzake preventie en hergebruik van afvalstoffen
Staatsuitgeverij, Den Haag
VROM (1988c)
Informatiebundel leder-, schoen- en andere lederwarenindustrie
Handhaving Milieuwetten no. 20
Staatsuitgeverij Den Haag
VROM (1988d)
Rapportage van de Werkgroep Verwijdering Zware Metalen uit Afvalwater